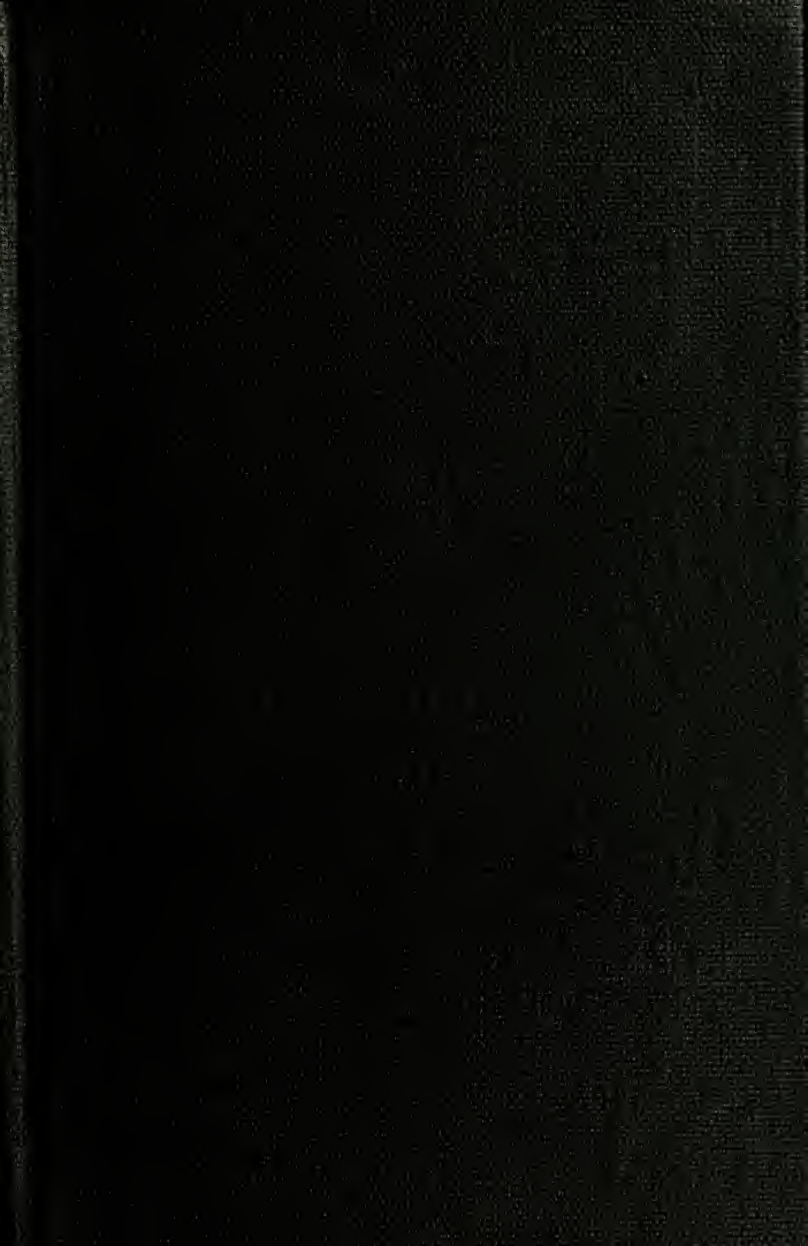


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PAPERS COMMUNICATED TO THE CHEMICAL SOCIETY.

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THE CHEMICAL SOCIETY.

TRANSACTIONS.

I.—*A Method for the Direct Production of Certain Aminoazo-compounds.*

By RAPHAEL MELDOLA, F.R.S., and LEWIS EYNON, B.Sc., F.I.C.

THE methods at present known for producing aminoazo-compounds of amines and phenols are the following:

(1) Intramolecular rearrangement of diazoamines (the original method of Mène, Martius, and Griess).

(2) The reduction of *p*-nitroazo-derivatives of amines and phenols by alkaline sulphides (Meldola, Trans., 1883, **43**, 425).

(3) The combination of a diazotised monoacetyl-diamine with an amine or phenol and subsequent hydrolysis of the acetyl derivative (Nietzki, *Ber.*, 1884, **17**, 343).

(4) The application of Bamberger's method—the action of nitrosobenzene on amines—to monoacetyl-diamines followed by hydrolysis of the acetyl derivative (Mills, Trans., 1895, **67**, 928).

(5) The alkaline reduction of nitroamines (Haarhaus, *Annalen*, 1865, **135**, 164; Mixter, *Amer. Chem. J.*, 1883, **5**, 283; Nietzki, *Ber.*, 1884, **17**, 345; Gräff, *Annalen*, 1885, **229**, 341; Nölting and Binder, *Ber.*, 1887, **20**, 3016; Meldola and Andrews, Trans., 1896, **69**, 10; Nölting and Fourneaux, *Ber.*, 1897, **30**, 2938).

This last process, which has been made the subject of many patents, is especially suitable for the production of diaminoazo-compounds.

In a note formerly published by one of the authors and W. A. Williams (Proc., 1899, **15**, 196), it was announced that *p*-aminobenzeneazophenol underwent fission in the presence of sodium dichromate and sulphuric acid with the formation of benzoquinone and a diazo-chromate. This observation was originally made in the course of experiments having for their object the preparation, if possible, of azoquinones of the type :

$$O:C_6H_4:N\cdot N:C_6H_4:O\ .$$

The research led to the conclusion that such compounds, if not incapable of existence, were at any rate not formed by any of the methods employed by us. The experiments were, however, continued with the object of investigating more closely the crystalline product of fission and oxidation obtained as above described. As already stated, this proved to be a mixture of benzoquinone and a diazo-(diazonium)-chromate, the remarkable stability of the latter making it appear a promising subject of investigation. The results, although worked out some years ago, have not hitherto been made known.

Decomposition of p-*Aminobenzeneazophenol.*

The aminoazo-compound or its sulphate (Meldola and Williams, *loc. cit.*) is suspended in dilute sulphuric acid, and to the well-cooled solution a strong solution of sodium dichromate is added drop by drop, until a distinct orange colour indicates the presence of an excess of the reagent. The sulphate of the azo-base at first dissolves, and after some hours yellow, scaly crystals are deposited. It is best to keep the beaker containing the solution in melting ice during the oxidation, and to employ a cold saturated solution of sodium dichromate. The crystalline deposit is collected, washed with water, and finally with alcohol to remove quinone. When dry, the diazonium chromate is very stable if kept in the dark. On exposure to light, it gradually becomes brown. The salt can be dissolved in boiling glacial acetic acid, and the solution, when rapidly cooled, deposits the unaltered compound in the form of dense orange scales. The exploding point of the pure salt is 144—148° ; the explosion is not particularly violent, and is followed by a cloud of woolly chromium sesquioxide.

0·0969 gave 14·4 c.c. moist nitrogen at 10·25° and 758·1 mm. N = 17·71.
0·1298 „ 20·25 c.c. „ „ 18° „ 759·7 mm. N = 17·99.
0·0876 „ 0·0269 Cr_2O_3. Cr = 21·0.
0·1541 „ 0·0324 Cr_2O_3. Cr = 20·99.
$NH_2\cdot C_6H_4\cdot N_2\cdot HCrO_4$ requires N = 17·72. Cr = 21·94 per cent.

The isolation of a diazonium salt of such stability from an aqueous solution appears to open up new possibilities with respect to the isolation of these hitherto somewhat unmanageable compounds. No salt of this amino-diazonium type has, so far as we know, been isolated up to the present time. A simple diazonium chromate, namely, that derived from aniline, was described many years ago by Caro and Griess (*Bull. Soc. Chim.*, 1867, [ii], **7**, 270), and its use as an explosive patented by these authors in France (Fr. Pat. No. 73286).

The composition of the salt having been established, it became obvious that a more direct method of preparing it in quantity would be to start from diazotised *p*-phenylenediamine, Griess having long ago pointed out that this and other diamines could be diazotised in well-cooled solutions in presence of a large excess of acid (*Ber.*, 1884, **17**, 607; 1886, **19**, 319). *p*-Phenylenediamine sulphate was thus found by us to give a good yield of the above chromate when suspended in an excess of dilute sulphuric acid, diazotised with the calculated quantity of sodium nitrite in the usual way, and then precipitated by the addition of a strong solution of sodium dichromate to the ice-cold solution of the diazonium sulphate.

Formation of Aminoazo-compounds.

Like all diazonium salts, the foregoing chromate interacts with amines and phenols, so that a direct method of producing aminoazo-compounds has now become possible, and may be added to the list of available processes given above. As a test case, the preparation of the *p*-aminobenzeneazo-β-naphthol described by one of the authors in 1885 (Meldola, Trans., 1885, **47**, 663) may be described. This compound was originally prepared by combining diazotised *p*-nitroaniline with β-naphthol in alkaline solution, and then reducing the *p*-nitroazo-compound with ammonium sulphide. In applying the present method, the solid diazonium chromate is simply added in small portions to a solution containing the calculated quantity of β-naphthol dissolved in dilute sodium hydroxide, the contents of the vessel in which the mixture is effected being briskly agitated after each addition. The amino-azo-compound is immediately precipitated, and the reaction is practically complete when the whole of the chromate has been added. The compound formed is identical with that described in 1885. As this compound does not possess any well marked specific characters, it was acetylated by heating for a few minutes on the water-bath with an excess of acetic anhydride. The acetyl derivative crystallises from alcohol in bright red needles melting at 259—260°.

0·1707 gave 0·4395 CO_2 and 0·0747 H_2O. C = 70·42 ; H = 4·88.
0·0670 „ 7·75 c.c. moist nitrogen at 13·8° and 772·2 mm. N = 13·83.
0·0948 „ 10·95 c.c. „ „ 13·4° „ 766·3mm. N = 13·72.
$C_2H_3O·NH·C_6H_4·N_2·C_{10}H_6·OH$ requires C = 70·72 ; H = 4·92 ; N = 13·77 per cent.

The same acetylaminoazo-compound is formed by combining diazoised acetyl-*p*-phenylenediamine with β-naphthol in the usual way.

The precipitation of crystalline chromates from solutions of more soluble diazonium salts is a very general property which in many cases may be found of special use, since no method for the direct precipitation of a diazonium salt with an inorganic acid radicle from an aqueous solution has hitherto been available excepting by the use of the costly platinic and auric chlorides. The salts obtained by the present method are directly available for all those reactions in which the presence of chromic acid is not prejudicial. In cases where the diazonium salt is not isolated, but combined when formed in aqueous solution with amines or phenols, as in all the technical processes for producing azo-colours, the chromates obviously offer no advantage. For scientific purposes, however, where a definite quantity of a diazonium salt has to be brought into reaction with some other compound, we believe that the chromates will be found to be very suitable. We have made preliminary experiments with many diazotisable bases, and with few exceptions the diazonium chromates are all distinctly crystalline salts possessed of greater or lesser stability. Thus the diazonium chromates of *p*-aminophenol, *p*-nitroaniline, *m*-nitroaniline, *p*-chloroaniline, *p*-bromoaniline, acetyl-*p*-phenylenediamine, aminoazobenzene, benzidine, tolidine, and the ethenyltriaminonaphthalenes (both isomerides) have all been isolated. They have not been studied in detail as yet and we make these results known by way of a preliminary communication, as some of these salts possess properties which may make it worth while submitting them to special investigation. Their composition appears to vary according to the nature of the organic radicle which they contain. Thus, diazotised *p*-aminophenol gives a crystalline salt which has the composition of a normal dichromate :

	Calculated for $[HO·C_6H_4·N_2]_2Cr_2O_7$.	Found.
C	31·44	31·89
H	2·18	2·50
N	12·23	12·75
Cr	22·71	23·35

The exploding point of this salt when pure is about 134°. It is less stable than the chromate from *p*-phenylenediamine, as it undergoes

decomposition on heating in glacial acetic acid solution. Some of the salts derived from other bases gave results on analysis which showed that they were complex chromates.

The salts are all more or less explosive when dry, and we think it desirable to call especial attention to this point in order that caution may be exercised by those who prepare them. The nitrodiazonium chromates explode with very great violence. None of the salts which we have tried explode by percussion, but only on ignition. It is possible that some of them may find technical application as high explosives.

CITY AND GUILDS OF LONDON TECHNICAL COLLEGE,
FINSBURY.

II.—*The Diazo-reaction in the Diphenyl Series. Part II. Ethoxybenzidine.*

By JOHN CANNELL CAIN.

IN an investigation on the action of heat on an acid solution of the diazonium salts derived from dianisidine and 3 : 3′-dichlorobenzidine (Trans., 1903, **83**, 688), it was shown that these substances behave very differently from the corresponding salts derived from benzidine and tolidine. Whereas, as is well known, the diazonium salts prepared from the two latter bases give the normal diazo-reaction and yield the corresponding hydroxy-compounds (diphenols) on boiling with dilute acid, thus:

$$\begin{matrix} C_6H_4\cdot N_2\cdot Cl \\ | \\ C_6H_4\cdot N_2\cdot Cl \end{matrix} \longrightarrow \begin{matrix} C_6H_4\cdot OH \\ | \\ C_6H_4\cdot OH \end{matrix} \text{ and } \begin{matrix} C_6H_3Me\cdot N_2\cdot Cl \\ | \\ C_6H_3Me\cdot N_2\cdot Cl \end{matrix} \longrightarrow \begin{matrix} C_6H_3Me\cdot OH \\ | \\ C_6H_3Me\cdot OH \end{matrix},$$

the yield being nearly quantitative.

A very different reaction apparently occurred in the case of the former pair of bases, thus, dianisidine gave no trace of a phenol and dichlorobenzidine yielded only a very slight amount of the dichlorodiphenol, the chief products being probably of a quinonoid nature.

The introduction of a methoxy-group or a chlorine atom in the ortho-position to the amino-group apparently has a great influence in modifying the course of the reaction, and it was obviously of much interest to investigate the mechanism of the reaction in the case of a similarly mono-substituted derivative. A difficulty at once, however, presented itself in that no chlorobenzidine is known, and methoxybenzidine is not readily procurable. The corresponding ethoxybenzidine is, however, prepared on the commercial scale, and in view

of the difficulty of preparing the methoxy-derivative it was thought that an investigation carried out with the ethoxy-compound would be of equal value; and, indeed, the interesting results obtained have confirmed this anticipation.

When the aqueous solution of the diazonium salt is boiled with dilute sulphuric acid, or when a current of steam is passed through its acid solution for some time, nitrogen is evolved, and, on cooling, long, brown, needle-shaped crystals separate out. After drying, these were found to contain sulphur in the form of sulphuric acid, which was easily removed by treatment with sodium carbonate, the substance being therefore a salt of this acid with some base. The substance when very carefully tested for nitrogen by the sodium method gave a negative result, but on making a nitrogen determination as much as 8 per cent. was found. The substance, when dissolved in water, combined instantly with β-naphthol, forming an azo-colouring matter, and its identification as a diazonium salt was thus complete. Analyses showed that one of the diazonium groups of the original tetrazo-salt had remained unattacked by boiling with dilute acid, whilst the other had been entirely replaced by the hydroxyl group. This one diazonium group is exceedingly stable, whereas the other is completely decomposed by boiling with dilute acid, exactly as in the case of the diazonium salt from benzidine. The question at once arises as to which diazonium group has been substituted: that in the ethoxyphenyl ring or that in the unsubstituted nucleus. Since the presence of the methoxy-group in the ortho-position with respect to the diazonium group very greatly increases the stability of the latter (compare Trans., 1902, 81, 1438), one is justified in concluding that in the case of the tetrazo-salt from ethoxybenzidine it is the diazonium complex next to the ethoxy-group which remains unattacked by boiling dilute acid under the conditions of the experiment. It should, however, be mentioned that prolonged boiling for many hours also effects the decomposition of this group, but the product has not been further examined.

The formation of the new substance may therefore be expressed as follows:

$$HSO_4{\cdot}\underset{\overset{\vdots}{N}}{N}\langle C_6H_4\rangle{-}\langle \overset{OEt}{C_6H_3}\rangle\underset{\overset{\vdots}{N}}{N}{\cdot}HSO_4 \longrightarrow HO\langle C_6H_4\rangle{-}\langle \overset{OEt}{C_6H_3}\rangle\underset{\overset{\vdots}{N}}{N}{\cdot}HSO_4.$$

This is, so far as I know, the first example of a substance containing two diazonium groups which undergoes such a change.

The diazonium sulphate is exceedingly stable, for when dried on a porous plate it may be preserved either in a desiccator or in the open air for months without undergoing any decomposition, except that on exposure to the light it becomes slightly darker in colour.

The free base obtained by neutralisation with sodium carbonate has been combined with different acids, the salts of which are described in the sequel, the details regarding the azo-derivatives and substitution products being reserved for a future communication.

Experimental.

4'-Hydroxy-3-ethoxydiphenyl-4-diazonium Sulphate.—The ethoxybenzidine used in these experiments was obtained from Messrs. L. Cassella and Co., Frankfort, and the author wishes to express his acknowledgment of the kindness of this firm in providing him with a quantity of this material.

The technical product is purified by extraction with benzene, the pure ethoxybenzidine being obtained from the filtered solution on evaporation. This base is then diazotised in the usual way; 15 grams are dissolved in hot water, acidified with 40 c.c. of concentrated hydrochloric acid, the solution cooled with ice to 5°, and an aqueous solution of 8·7 grams of sodium nitrite added. The ethoxybenzidine is thus completely diazotised, both amino-groups being changed into diazonium groups. The diazo-solution is now poured into a mixture of 60 c.c. of sulphuric acid and 120 c.c. of water, and heated to boiling, either over the free flame or by the introduction of a current of steam, until the evolution of nitrogen has ceased. This operation may take half an hour. The hot solution is allowed to cool, when long, needle-shaped crystals separate out, which are collected and dried on a porous plate, the yield being about 14 grams. The crystals in this form are dark brown, but when powdered the product exhibits an orange-brown tint.

The hot solution may also be separated with common salt when the diazonium sulphate is precipitated as a yellow powder. The diazonium salt thus prepared may be recrystallised from boiling dilute sulphuric acid. It is easily soluble in water, forming a pale yellow solution, which combines at once with "R salt," forming a violet azo-compound.

When dried in the air on a porous plate, the sulphate contains two molecules of water, which are eliminated by drying in a desiccator over sulphuric acid; the anhydrous salt is thus obtained without any change of colour being observed. If, however, the hydrated salt is dried at 100°, it turns green and undergoes decomposition.

0·2092 gave 0·3446 CO_2 and 0·0927 H_2O. C = 44·93; H = 4·92.
0·2192 „ 0·3620 CO_2 „ 0·0859 H_2O. C = 45·03; H = 4·35.
0·2051 „ 0·12283 $BaSO_4$. S = 8·22.
2·5 lost, over sulphuric acid, 0·2692 H_2O. H_2O = 10·77.

$C_{14}H_{14}O_6N_2S,2H_2O$ requires C = 44·92; H = 4·81; S = 8·55; H_2O = 9·6 per cent.

The anhydrous salt gave the following numbers :

0·2889 gave 0·5252 CO_2 and 0·1118 H_2O. C = 49·58 ; H = 4·30.
0·1963 „ 0·13193 $BaSO_4$. S = 9·23.
0·2596 „ 18·4 c.c. nitrogen at 15° and 750 mm. N = 8·35.
$C_{14}H_{14}O_6N_2S$ requires C = 49·70 ; H = 4·14 ; S = 9·46 ; N = 8·28 per cent.

Both the hydrated and anhydrous salts dissolved easily in cold water, giving a light yellow solution which, on the addition of aqueous sodium carbonate, yielded a lilac-coloured precipitate, this being soluble in excess of alkali to form a blood-red solution. On acidifying with hydrochloric acid, the lilac-coloured compound did not re-appear, but a green precipitate resulted which was insoluble in excess of acid and was not further examined.

The lilac-coloured precipitate thus obtained is the free diazonium hydroxide, $HO\cdot C_6H_4\cdot C_6H_3(OEt)\cdot N(OH)⋮N$, or possibly its anhydride,

$$\begin{matrix} C_6H_4O\text{---} \\ | \\ C_6H_3(OEt) \end{matrix} > N⋮N.$$

This substance was dried over sulphuric acid, but a subsequent analysis showed that decomposition had taken place. For the preparation of the different salts, the base was isolated as a paste and then dissolved in the hot dilute acid, the corresponding salt crystallising out on cooling.

The *diazonium chloride* crystallises from the hot solution in fine golden-brown needles.

0·1329 gave 0·2852 CO_2 and 0·0563 H_2O. C = 58·53 ; H = 4·70.
0·2030 „ 0·10393 AgCl. Cl = 12·66.
0·1655 „ 0·08653 AgCl. Cl = 12·93.
$C_{14}H_{13}O_2N_2Cl$ requires C = 60·78 ; H = 4·70 ; Cl = 12·80 per cent.

The *diazonium bromide* crystallises from the hot solution of the base in dilute hydrobromic acid in fine golden-yellow needles. After drying over sulphuric acid, the salt had turned brown on the surface, so that the rather high percentage of bromine found on analysis is probably due to a slight decomposition.

0·1946 gave 0·12123 AgBr. Br = 26·52.
$C_{14}H_{13}O_2N_2Br$ requires Br = 24·92 per cent.

The *diazonium iodide* is a dull yellow powder, which is still more unstable than the bromide and must be prepared without the aid of heat by triturating the base with cold hydriodic acid. After drying in a desiccator, the salt had become green on the surface, this slight amount of decomposition accounting for the high value obtained in the iodine estimation.

0·1568 gave 0·10403 AgI. I = 35·84.
$C_{14}H_{13}O_2N_2I$ requires I = 34·48 per cent.

The *diazonium nitrate* crystallises from the hot solution in clusters of reddish-yellow needles. Like the sulphate and chloride, it is fairly stable and remains unchanged in the desiccator.

0·2162 gave 26·5 c.c. nitrogen at 20° and 754 mm. N = 14·28.
$C_{14}H_{13}O_5N_3$ requires N = 13·86 per cent.

The *platinichloride* is obtained as a canary-yellow precipitate on adding platinic chloride to a solution of the diazonium chloride.

0·1109 gave 0·0230 Pt. Pt = 20·74.
$(C_{14}H_{12}O_2N_2)_2,H_2PtCl_6$ requires Pt = 21·90 per cent.

III.—*The Sulphate and the Phosphate of the Dimercurammonium Series.*

By Prafulla Chandra Rây.

The preparation of dimercurammonium nitrite, NHg_2NO_2, having already been described (Trans., 1902, **81**, 644), it occurred to me that by treating this compound with an acid, the NO_2 group would be destroyed and the corresponding salt of the reacting acid would be formed. It was, however, found that a halogen acid completely breaks up the molecular structure, giving rise to double salts of the type $2NHg_2X,NH_4X$, where X represents a halogen atom; but on substituting nitric acid for the halogen acid, the nitrate of the series was readily obtained (*Zeit. anorg. Chem.*, 1902, **33**, 209). It therefore seemed probable that an oxy-acid would behave differently from a halogen acid.

Acting on this hint, I have lately treated dimercurammonium nitrite with sulphuric and phosphoric acids respectively, and have succeeded in preparing the corresponding salts.

The Sulphate.—Dimercurammonium nitrite is gently heated to boiling for some time with dilute sulphuric acid, when nitrous fumes are liberated. As both the parent substance and its derivatives are insoluble, prolonged digestion is necessary before the NO_2 group is completely removed. A white, bulky, crystalline powder is obtained, which is washed free from the adhering mother liquor and dried in the steam-oven. The sulphate thus prepared is soluble in hydrochloric acid and conforms to the formula $(NHg_2)_2SO_4,H_2O$.

	Calculated.	Found. I.	Found. II.
Hg	84·92	84·00	—
N	2·97	3·26	—
SO_4	10·19	10·96	10·21
H_2O	1·92	—	—

The foregoing analyses were made with different preparations. The salt gives off moisture when heated in a bulb tube.

The Phosphate.—This salt is prepared in much the same way as the sulphate; it is only necessary to lay stress on the fact that as phosphoric acid attacks the NO_2 group much more slowly than sulphuric acid, continued digestion at 50—60° for 2 to 3 days has been found to be necessary.

The salt is obtained as a white, crystalline powder, which is washed and dried just as in the case of the sulphate; it has the formula NHg_2,H_2PO_4. The analyses given below were made with three distinct preparations.

	Calculated.	Found. I.	Found. II.	Found. III.
Hg	78·30	78·54	77·4	78·07
N.	2·74	2·00	—	—
P	6·07	6·44	6·33	—

It has all along been pointed out that when mercury is directly attached to the nitrogen atom, a more stable compound is formed than when it is linked to nitrogen through the intermediary of an oxygen atom, and this is strikingly shown in the behaviour of sodium sulphate towards mercuric nitrite and nitrate respectively (Trans., 1897, **71**, 1103). It is also well known that a haloid of mercury is attacked by sulphuric acid with considerable difficulty. The "nitronic" or haloid constitution of the salts in both cases goes to account for this resistance of the SO_4 ion. In the dimercurammonium complex, NHg_2, also, owing to the nitrogen atom being directly related to the mercury atoms, the molecular structure remains unaffected when the salt is subjected to the action of an oxy-acid, but at once succumbs to the attack of a halogen acid.

It is also of interest to note that whilst both the hydrogen atoms of sulphuric acid are replaced by the group NHg_2, only one atom of the tribasic phosphoric acid is similarly affected. This is what might have been expected, considering that in ordinary circumstances even a strong base like caustic soda can only yield the disodium phosphate.

The Davy-Faraday Research Laboratory,
The Royal Institution.

IV.—*The Viscosity of Liquid Mixtures. Part II.*

By Albert Ernest Dunstan, B.Sc.

In Part I of this investigation (Trans., 1904, **85**, 817, and *Zeit. physiol. Chem.*, 1904, **49**, 590), I gave an account of the variation of absolute viscosity with concentration in the cases of the following pairs of liquids: 1, benzene—ethyl acetate; 2, ethyl alcohol—carbon disulphide; 3, mercaptan—ethyl alcohol; 4, acetone—ethyl alcohol; 5, benzene—ethyl alcohol; 6, benzaldehyde—ethyl alcohol; 7, ethyl alcohol—water; 8, methyl alcohol—water; and 9, acetic acid—water. The curves thus obtained could be divided into three classes: 1, sagged curves, approximating to the normal (Nos. 1, 2, 3, and 4); 2, curves showing minimal values of viscosity (Nos. 5 and 6), and 3, curves giving one or more maximal values of viscosity (Nos. 7, 8, and 9).

Based on the fact that hydroxylated, associated liquids such as water and the alcohols have a relatively high value of viscosity, the conclusion was deduced that a maximum point in a viscosity-concentration curve meant further association proceeding in the components, whilst the existence of a minimum point pointed to the opposite view, namely, that some dissociation had resulted. Further experiments bear out the conclusion arrived at in the former paper.

The apparatus has been modified in various ways with the result that a higher degree of accuracy has been attained. A large copper rectangular tank provided with windows is used as the bath. The viscometers are much larger and are employed in duplicate, one for mixtures of high, and the other for those of low viscosity. Larger specific gravity tubes have been employed, having a capacity of 10 c.c. The liquids used, which were obtained from Kahlbaum, have been carefully rectified and fractionated, and the components of the various mixtures have been weighed out to the milligram.

Experimental.

1. *Allyl Alcohol* (sp. gr. 0·8500 at 25°/0°) *and Water.*

The curve afforded by this pair of liquids is of precisely the same form as was given by ethyl alcohol—water and methyl alcohol—water. There is a very well-marked maximum at 51—52 per cent. of allyl alcohol corresponding with 1 allyl alcohol, 3 water; at this point, the viscosity of the mixture is 0·01895, or about twice that of water. It is somewhat remarkable that, in the two cases just quoted, there are also maxima at 1 alcohol, 3 water.

There is also a distinct indication of a discontinuity at 40 per cent.

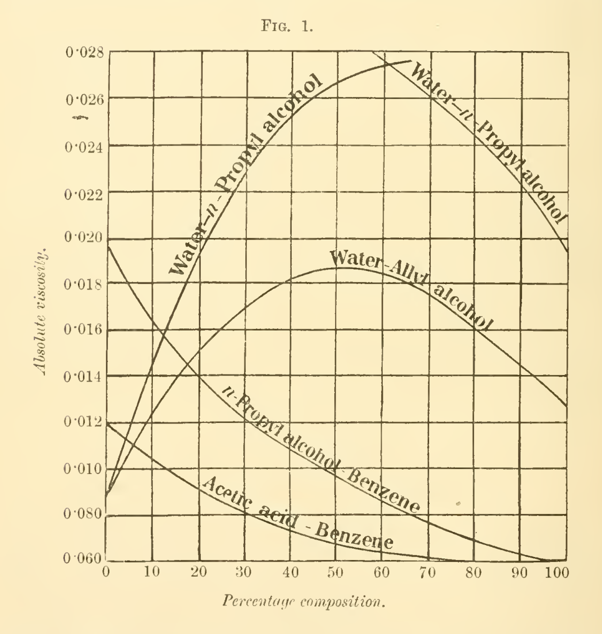
of allyl alcohol; at this concentration, the molecular proportions are 1 allyl alcohol, 5 water.

Allyl alcohol. %	η.	Allyl alcohol. %	η.
0·0	0·00891	47·31	0·01887
100·0	0·01232	47·82	0·01891
14·06	0·01349	48·56	0·01892
25·98	0·01682	56·63	0·01891
33·70	0·01789	65·00	0·01796
35·53	0·01834	69·56	0·01750
36·53	0·01846	83·20	0·01537
45·21	0·01888		
46·88	0·01895		

2. n-*Propyl Alcohol* (sp. gr. 0·8009 at 25°/4°) *and Water.*

Again, as in previous cases of alcoholic solution in water, a very great rise in viscosity takes place on mixing the components. A

FIG. 1.



clearly marked maximum occurs at 61—62 per cent. of *n*-propyl alcohol, corresponding with 1 propyl alcohol, 2 water.

At this point, the viscosity of the mixture is 0·02725, which is not

so far removed from that of the alcohol as appears from the curves for methyl and ethyl alcohols.

The viscosities of methyl, ethyl, and propyl alcohols are 0·005564, 0·01113, and 0·01962 respectively, whereas the maximum values for the corresponding mixtures in water are 0·01600, 0·02368, and 0·02725.

n-Propyl alcohol. %	η.	*n*-Propyl alcohol. %	η.
0·0	0·00891	43·40	0·02616
8·55	0·01289	52·90	0·02686
9·29	0·01312	53·58	0·02707
22·61	0·01982	64·94	0·02703
24·91	0·02047	69·40	0·02620
25·59	0·02110	69·87	0·02605
28·31	0·02188	79·43	0·02450
35·15	0·02456	83·89	0·02364
36·42	0·02438	86·60	0·02311
		100·0	0·01962

3. *Glycol* (sp. gr. 1·1110 at 25°/0°) *and Water.*

Contrary to expectation, this mixture did not provide a curve which agreed with those afforded by other hydroxylated compounds in aqueous solutions. A few preliminary experiments with glycerol also gave negative results and were abandoned. Graham in his classical paper on viscosity found a similar occurrence with glycerol (compare Trans., *loc. cit.*). So far from further association taking place, the reverse is indicated. It is quite possible that this substance, being already greatly associated in consequence of its two hydroxyl groups (as is shown by its very high coefficient of viscosity), is broken down by the water into simpler complexes. It would, therefore, be interesting to ascertain the magnitude of its "molecular weight" at varying concentration, using the depression of freezing point of the aqueous solutions.

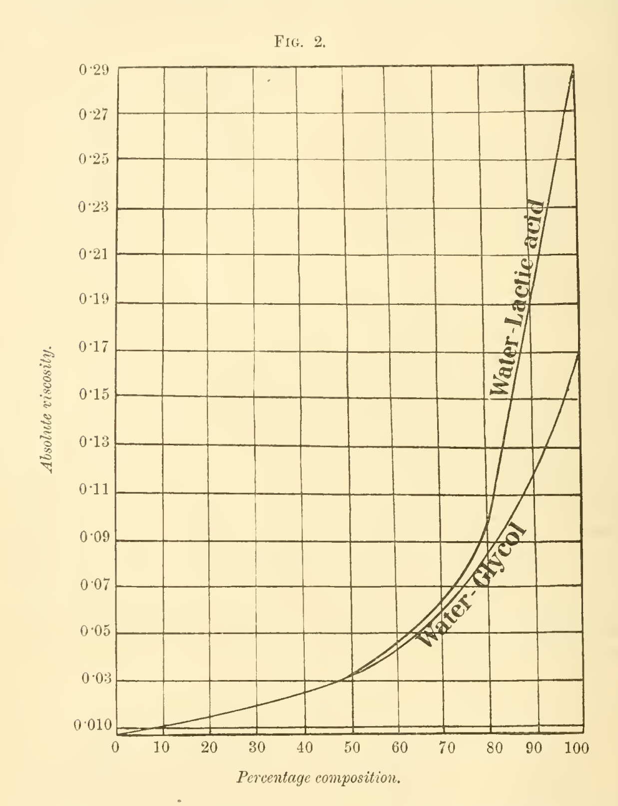
Glycol. %	η.	Glycol. %	η.
0·0	0·00891	60·84	0·04488
14·11	0·01258	69·52	0·06227
33·11	0·01621	75·64	0·09202
45 13	0·02860	100·0	0·1733
49·55	0·03199		

The greatest divergence from the normal occurs at about 64 per cent. of glycol, this point corresponding with 1 glycol, 2 water.

4. *Lactic Acid* (sp. gr. 1·2060 at 25°/4°) *and Water.*

This hydroxy-acid has a different behaviour from that of acetic acid. No maximum point is observed, whereas that of acetic acid is markedly

FIG. 2.



prominent. On the contrary, a very sagged curve is obtained, giving a maximal divergence with about 70 per cent. of lactic acid, corresponding with 1 lactic acid, 2 water.

Again, it seems probable that this very viscous, dihydroxylated substance breaks down in the presence of water to a simpler complex, as was noticed in the case of glycol and glycerol.

Lactic acid. %.	η.	Lactic acid. %.	η.
0·0	0·00891	43·98	0·02733
12·76	0·01186	53·30	0·03591
21·71	0·01455	60·24	0·03621
30·85	0·01849	75·75	0·07995
33·69	0·01782	100·0	0·4033
34·76	0·02026		

5. *Benzene and Acetic Acid* (sp. gr. 0·8738 and 1·047 at 25°/4° respectively).

Considering the fact that acetic acid in benzene solution gives abnormal results for the depression of freezing point, leading to the supposition that it contains double molecules, it seemed of interest to study the behaviour of mixtures of these substances from the standpoint of viscosity, particularly as mixtures of benzene and ethyl alcohol afford a minimum point (Trans., *loc. cit.*).

A specimen of pure acetic acid had been previously obtained by freezing out some of Kahlbaum's acid. This boiled at 117·8°/752 mm., and by the freezing point method was found to contain 99·9 per cent. of acetic acid. It was thought that this very small trace of impurity would not affect the results to any appreciable extent.

The benzene used was supplied by Merck; it was distilled over sodium and boiled entirely between 80° and 81°. Alternate readings from two stop-watches were taken in all the following experiments, and they have been found to agree to a very satisfactory extent. The time of flow for benzene is only 3′25″, so that an accuracy greater than 1 in the third place of decimals is scarcely attainable.

A distinct minimum was obtained at 89 per cent. of benzene corresponding with 5 benzene, 1 acetic acid. This minimal value is 2 per cent. below that for acetic acid and seems to indicate a certain amount of dissociation. By the freezing point method, a distinct tendency is shown for the formation of complex molecules (compare Walker, *Introduction to Physical Chemistry*, p. 204).

Grams of acetic acid in 100 grams of benzene......	0·465	1·195	2·321	4·470	8·159
Molecular weight	110	115	117	122	129

It is not known, however, what is the molecular complexity of pure acetic acid in the liquid condition and at the ordinary temperature. It is quite possible, however, that its complexity is greater than $2C_2H_4O_2$, for instance, so that although in dilute solution in benzene it is approximately bimolecular, yet this condition may result from the breaking down of a more complex molecule.

Benzene. %.	η.	Benzene. %.	η.
0·0	0·01174	81·42	0·005962
16·74	0·008932	89·73	0·005907
34·93	0·007341	97·25	0·005941
48·29	0·006658	100·0	0·005978
77·26	0·005969		

6. *Benzene and* n-*Propyl Alcohol* (sp. gr. 0·8728 and 0·8009 at 25°/4° respectively).

The foregoing result with benzene and acetic acid and the previous case of benzene and ethyl alcohol made it of interest to investigate other benzene solutions. Although with benzene and *n*-propyl alcohol the minimum is not so well marked, it clearly exists, being about 1 per cent. below the value for benzene. It occurs at 95 per cent. of benzene, corresponding with 12 benzene, 1 propyl alcohol.

n-Propyl alcohol. %.	η.	*n*-Propyl alcohol. %.	η.
0·0	0·01962	89·99	0·005989
33·10	0·01167	95·07	0·005917
70·22	0·007028	100·0	0·005978

Preliminary experiments with mixtures of benzene and methyl alcohol gave similar results.

Summary.

Hydroxylated compounds give abnormal results, but, in the case of polyhydroxylated liquids this abnormality does not exist, probably because of the large degree of association originally existing in such substances. Discontinuities in the curves locate themselves at or near points of definite molecular composition, and this occurs so frequently that one is compelled to recognise the existence in solution of molecular aggregates such as 1 ethyl alcohol, 3 water.

On the other hand, abnormalities occur when hydroxylated substances are dissolved in benzene, but here they are opposite in nature, minimum points being obtained, a fact which indicates that the molecular complexes are disturbed in this solvent, although, in the case of organic acid, the solute is not broken down to the monomolecular condition.

At present there is no well-defined molecular constant of viscosity, owing perhaps to the large variation of viscosity with temperature and the difficulties of finding corresponding temperatures, and consequently it is not possible to find the molecular condition of a liquid by determining its coefficient of viscosity, but from a qualitative point of view it is obvious that associated substances are more viscous than mono-

molecular substances. That there is a distinct difference between the two classes of substances may be seen from the following table, which gives the quotient of molecular volume by viscosity for the different compounds:

Ethyl acetate	29700	Mono-molecular liquids.	Methyl alcohol	7240	Associated liquids.
Benzene	15300		Ethyl ,,	4930	
Carbon disulphide	16600		Water	2020	
Ethyl mercaptan	35400		Benzaldehyde	6840	
			Acetone	23400	
			Acetic acid	4970	

Taking into account the foregoing consideration, it is quite clear that (with the exception of acetone) the associated liquids stand in a class by themselves (compare Thorpe and Rodger, *J. Phil. Trans.*, 1894, II., A. 185).

The author intends to extend this research to other hydroxylated compounds.

OWEN'S SCHOOL,
ISLINGTON, N.

V.—*The Combination of Mercaptans with Olefinic Ketonic Compounds.*

By SIEGFRIED RUHEMANN.

SINCE Baumann carried out his important researches on the mercaptoles, it has been Posner especially who has studied the interaction of mercaptans with ketones and has applied it to olefinic ketones (*Ber.*, 1901, **34**, 1395; 1902, **35**, 799; 1904, **37**, 502). His experiments led to the result that mercaptans, besides condensing with the ketonic group of the mono-olefinic ketones, also became attached to the ethylene linking, and thus yielded trithio-compounds, for instance:

$$C_6H_5\cdot CH\colon CH\cdot CO\cdot CH_3 + 3C_5H_{11}\cdot SH = C_6H_5\cdot CH(S\cdot C_5H_{11})\cdot CH_2\cdot C(S\cdot C_5H_{11})_2\cdot CH_3.$$

He arrived, however, at the conclusion that, although the mercaptans united by addition with all the mono-olefinic ketones, the tendency of the mercaptole reaction to take place was diminished if the ketonic group was adjacent to the ethylenic linking. This inhibiting influence of the ethylenic linking he found to increase with the accumulation of alkyl groups, especially of phenyl radicles in the olefinic ketone. Thus, benzylidenedeoxybenzoin, $C_6H_5\cdot CH\colon C(C_6H_5)\cdot CO\cdot C_6H_5$, he showed, did not form a mercaptole, the mercaptans simply combining additively at

the ethylenic linking. Posner further stated that diolefinic ketones of the type $\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{:}\overset{|}{\mathrm{C}}\cdot\mathrm{CO}\cdot\overset{|}{\mathrm{C}}\mathrm{:}\overset{|}{\underset{|}{\mathrm{C}}}$ yielded additive products with 2 molecules of the mercaptans; sometimes, however, along with the additive change, the mercaptole reaction took place, but the tetrathio-compounds thus formed on oxidation were transformed into ketodisulphones. His experiments on diolefinic ketones containing the grouping $\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{:}\overset{|}{\mathrm{C}}\cdot\overset{|}{\mathrm{C}}\mathrm{:}\overset{|}{\mathrm{C}}\cdot\mathrm{CO}$– led him to the view that they do not form mercaptoles, but additive products with 2 molecules of mercaptans.

To bring about the action of mercaptans on the olefinic ketones, Posner either used hydrogen chloride alone or employed this agent together with zinc chloride in order to facilitate the condensation of the mercaptans with the ketonic group. With the view of preventing the mercaptans from reacting with the ketonic group and to effect only the combination of the mercaptans with the olefinic ketone, I have chosen bases as catalytic agents instead of hydrogen chloride. In my first experiments, sodium ethoxide was employed, but I have found since that piperidine acts more promptly; the reaction takes place with development of heat, yielding additive products only. These substances do not give a coloration with ferric chloride, they dissolve in cold concentrated sulphuric acid, forming yellow or orange solutions. On applying this reaction to a diolefinic ketone of the type I: $\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{:}\overset{|}{\mathrm{C}}\cdot\mathrm{CO}\cdot\overset{|}{\mathrm{C}}\mathrm{:}\overset{|}{\underset{|}{\mathrm{C}}}$, namely, dibenzylideneacetone, I find that either 1 or 2 molecules of a mercaptan may become attached. With regard to the action of mercaptans on diolefinic ketones of the type II: $\overset{|}{\underset{|}{\mathrm{C}}}\mathrm{:}\overset{|}{\mathrm{C}}\cdot\overset{|}{\mathrm{C}}\cdot\overset{|}{\mathrm{C}}\cdot\mathrm{CO}$–, I arrive, however, at a result which differs from that which Posner has obtained. As mentioned before, he found that cinnamylideneacetone as well as cinnamylideneacetophenone under the influence of hydrogen chloride takes up 2 molecules of a mercaptan, whilst I find that, on using piperidine as catalytic agent, cinnamylideneacetophenone, an example of the type of ketones hitherto examined by me, united with 1 molecule only of either phenyl or *iso*amyl mercaptan. It would therefore seem that the additive action of mercaptans on cinnamylideneacetophenone and olefinic ketones of similar constitution varies according as hydrogen chloride or piperidine is used as catalytic agent. I may, however, point out that if Posner's results are correct, the action of mercaptans would differ most markedly from the behaviour of other compounds towards olefinic ketones. Knoevenagel (*Ber.*, 1904, **37**, 4038), for instance, has lately shown that although diolefinic ketones with the grouping I, on treatment with potassium hydrogen sulphite, yield bishydrosulphonic acids, those of type II unite with 1 molecule of the hydrogen sulphite

only. But the following fact induces me to doubt the correctness of Posner's results. With one exception, he records only the analyses and properties of disulphones which he obtained by the oxidation of the products of the union of mercaptans with cinnamylideneacetone and cinnamylideneacetophenone respectively. The additive compound described by him (*Ber.*, 1904, **37**, 510) is the substance which he prepared from cinnamylideneacetophenone and phenyl mercaptan, and from the estimation of sulphur he concludes that it has the formula $C_6H_5\cdot CH(S\cdot C_6H_5)\cdot CH_2\cdot CH(S\cdot C_6H_5)\cdot CH_2\cdot CO\cdot C_6H_5$. The melting point (102°) of this substance, however, closely agrees with 103—104°, which I find to be the melting point of the product of the reaction of piperidine on the mixture of the ketone and the mercaptan. I have proved that the formula for this product is

$$C_6H_5\cdot CH\colon CH\cdot CH(S\cdot C_6H_5)\cdot CH_2\cdot CO\cdot C_6H_5,$$

and, moreover, having repeated Posner's experiment, I have ascertained that the compounds obtained by the two methods are identical.

The constitution of the substance which is formed from cinnamylideneacetophenone and phenyl mercaptan may be expressed either by the formula :

$$\text{I. } C_6H_5\cdot CH\colon CH\cdot CH(S\cdot C_6H_5)\cdot CH_2\cdot CO\cdot C_6H_5,$$

or, in the light of Thiele's hypothesis, it may be formulated as follows :

$$\text{II. } C_6H_5\cdot CH(S\cdot C_6H_5)\cdot CH\colon CH\cdot CH_2\cdot CO\cdot C_6H_5.$$

I am, however, inclined to attribute to it the former formula, and the analogous constitution to the substance which I have obtained from cinnamylideneacetophenone and *iso*amyl mercaptan, because both additive compounds dissolve in cold concentrated sulphuric acid, yielding a deep red solution, as do the diolefinic ketone itself and cinnamylidenemalonic acid and cinnamylideneacetylacetone.

Finally, it may be mentioned that the olefinic ketones seem to react not only with mercaptans, but also with hydrogen sulphide. As yet, I have examined only the behaviour of this gas towards benzylideneacetylacetone in the presence of sodium ethoxide, and have found that thiobenzaldehyde is produced. Its formation is most likely the result of the decomposition of the first formed additive product, and takes place thus : $C_6H_5\cdot CH(SH)\cdot CH(CO\cdot CH_3)_2 = C_6H_5\cdot CHS + CH_2(CO\cdot CH_3)_2$. This reaction, therefore, resembles the transformation of the additive products of olefinic ketones with primary organic bases (Ruhemann and Watson, Trans., 1904, **85**, 1170).

Experimental.

Action of Mercaptans on Mono-olefinic Ketonic Compounds.

Phenylthiolbenzylacetone, $C_6H_5 \cdot CH(S \cdot C_6H_5) \cdot CH_2 \cdot CO \cdot CH_3$.

Benzylideneacetone (2·6 grams) dissolves in slightly warm phenyl mercaptan (2 grams). On adding 2—3 drops of piperidine to the solution, it becomes hot, and in a short time sets to a hard solid. This is sparingly soluble in light petroleum (b. p. 50—60°) and crystallises from its solution in dilute alcohol in colourless needles which melt at 58—59°.

0·2018 gave 0·5545 CO_2 and 0·1155 H_2O. C = 74·93 ; H = 6·35.
$C_{16}H_{16}OS$ requires C = 75·00 ; H = 6·25 per cent.

This substance dissolves in cold concentrated sulphuric acid, yielding a green solution with a red fluorescence, but the colour slowly changes to red.

Ethyl Phenylthiolbenzylacetoacetate,
$C_6H_5 \cdot CH(S \cdot C_6H_5) \cdot CH(CO \cdot CH_3) \cdot CO_2 \cdot C_2H_5$.

The union of phenyl mercaptan with ethyl benzylideneacetoacetate has been brought about by means of a small quantity of an alcoholic solution of sodium ethoxide. When this is added to the mixture of the mercaptan (2 grams) and the freshly distilled ketonic ester (4 grams), the reaction takes place with development of heat, and, when cold, the whole solidifies. The substance readily dissolves in alcohol, chloroform, ether, or carbon disulphide, with difficulty, however, in light petroleum, and crystallises from this solution in colourless needles which melt at 72—73°.

0·2025 gave 0·5165 CO_2 and 0·1146 H_2O. C = 69·56 ; H = 6·28.
$C_{19}H_{20}O_3S$ requires C = 69·51 ; H = 6·10 per cent.

The solution of this compound in cold concentrated sulphuric acid is orange.

Ethylthiolbenzylacetylacetone, $C_6H_5 \cdot CH(S \cdot C_2H_5) \cdot CH(CO \cdot CH_3)_2$.

Benzylideneacetylacetone (3 grams) interacts with ethyl mercaptan (1 gram) on adding a few drops of an alcoholic solution of sodium ethoxide. The solid which is formed, is washed with water and dissolved in hot dilute alcohol ; the solution, on cooling, deposits colourless, silky needles, which melt at 75—76° and dissolve in cold concentrated sulphuric acid, yielding a light yellow solution.

0·2003 gave 0·4943 CO_2 and 0·1335 H_2O. C = 67·30; H = 7·40.
$C_{14}H_{18}O_2S$ requires C = 67·20; H = 7·20 per cent.

iso*Amylthiolbenzylacetylacetone*, $C_6H_5·CH(S·C_5H_{11})·CH(CO·CH_3)_2$.

The union of benzylideneacetylacetone (1·8 grams) and *iso*amyl mercaptan (1 gram) has been effected by sodium ethoxide dissolved in alcohol. The solid, which is produced after a few hours, dissolves in boiling light petroleum, and, on cooling, crystallises in colourless needles which melt at 57—58°.

0·2018 gave 0·5159 CO_2 and 0·1495 H_2O. C = 69·85; H = 8·24.
$C_{17}H_{24}O_2S$ requires C = 69·86; H = 8·22 per cent.

The solution of this substance in cold concentrated sulphuric acid is yellow.

Benzylthiolbenzylacetylacetone, $C_6H_5·CH(S·CH_2·C_6H_5)·CH(CO·CH_3)_2$.

This compound is formed on adding a few drops of sodium ethoxide dissolved in alcohol to the mixture of benzylideneacetylacetone (3 grams) and benzyl mercaptan (2 grams). The white solid, which separates on stirring, readily dissolves in hot alcohol, and, on cooling, crystallises in colourless prisms which melt at 77—78° and dissolve in cold concentrated sulphuric acid, yielding a deep yellow solution.

0·2024 gave 0·5429 CO_2 and 0·1175 H_2O. C = 73·15; H = 6·45.
$C_{19}H_{20}O_2S$ requires C = 73·08; H = 6·41 per cent.

Phenylthiolbenzylacetylacetone, $C_6H_5·CH(S·C_6H_5)·CH(CO·CH_3)_2$.

On adding a small quantity of sodium ethoxide dissolved in alcohol to the mixture of phenyl mercaptan (3 grams) and benzylideneacetylacetone (5 grams), heat is developed, and the whole becomes solid. This product, after washing with a little cold alcohol, is dissolved in boiling alcohol; the solution, on cooling, deposits colourless needles, which are readily soluble in ether, chloroform, or carbon disulphide, but less so in alcohol; the substance melts at 119—120°, and its solution in cold concentrated sulphuric acid is orange.

0·2012 gave 0·5347 CO_2 and 0·1112 H_2O. C = 72·47; H = 6·14.
0·3183 „ 0·2540 $BaSO_4$. S = 10·96.
$C_{18}H_{18}O_2S$ requires C = 72·48; H = 6·04; S = 10·74 per cent.

Phenylthiolbenzylbenzoylacetone,
$C_6H_5·CH(S·C_6H_5)·CH(CO·CH_3)·CO·C_6H_5$.

The union of benzylidenebenzoylacetone with phenyl mercaptan has been effected by mixing the diketone (4·5 grams) dissolved in benzene

with the mercaptan (2 grams) and adding 2—3 drops of piperidine, when, in a short time, the whole sets to a solid mass. This is washed with light petroleum and crystallised from alcohol, in which it dissolves with difficulty; colourless needles are thus obtained, which melt at 140—141° and dissolve in cold concentrated sulphuric acid, yielding an orange solution.

0·2008 gave 0·5640 CO_2 and 0·1016 H_2O. C = 76·63 ; H = 5·62.
$C_{23}H_{20}O_2S$ requires C = 76·76 ; H = 5·55 per cent.

iso*Amylthiolbenzylbenzoylacetone*,
$C_6H_5{\cdot}CH(S{\cdot}C_5H_{11}){\cdot}CH(CO{\cdot}CH_3)CO{\cdot}C_6H_5$.

The action of piperidine on a mixture of benzylidenebenzoylacetone (2·4 grams) and *iso*amyl mercaptan (1 gram) dissolved in light petroleum is accompanied by development of heat. The solid which is produced, is readily soluble in benzene or ether, less so in cold alcohol, but readily when hot, and crystallises from dilute alcohol in colourless needles which melt at 104—105°.

0·2005 gave 0·5466 CO_2 and 0·1326 H_2O. C = 74·35 ; H = 7·34.
$C_{22}H_{26}O_2S$ requires C = 74·57 ; H = 7·34 per cent.

The solution of this substance in concentrated sulphuric acid is yellow.

Action of Mercaptans on Diolefinic Ketones.

The Union of Dibenzylideneacetone with Mercaptans.

As already mentioned in the introduction, the union of mercaptans with dibenzylideneacetone yields either mono- or di-thio-compounds. The additive products, with 2 molecules of mercaptans, which Posner (*loc. cit.*) has already prepared, can readily be obtained in a pure state by the use of piperidine as catalytic agent instead of hydrogen chloride. But some difficulty may be experienced in getting the monothio-compounds pure, since their formation is accompanied by that of the additive products with 2 molecules of mercaptans. This is especially the case in the preparation of thiophenylbenzylbenzylideneacetone, which I have not yet obtained free from dithiophenyldibenzylacetone.

iso*Amylthiolbenzylbenzylideneacetone*,
$C_6H_5{\cdot}CH(S{\cdot}C_5H_{11}){\cdot}CH_2{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_5$.

This substance is formed by mixing *iso*amyl mercaptan (0·5 gram) with dibenzylideneacetone (1·2 grams) dissolved in benzene, and adding 3 drops of piperidine. After several hours, the benzene is

evaporated *in vacuo*, and, on stirring the residual oil, it solidifies. The solid is readily soluble in benzene, chloroform, ether, or alcohol, and crystallises from dilute alcohol in colourless needles which melt at 60—61°.

0·2024 gave 0·5788 CO_2 and 0·1405 H_2O. C = 77·99; H = 7·71.
$C_{22}H_{26}OS$ requires C = 78·10; H = 7·69 per cent.

The solution of this compound in concentrated sulphuric acid is yellow.

Phenylthiolbenzylbenzylideneacetone,
$C_6H_5{\cdot}CH(S{\cdot}C_6H_5){\cdot}CH_2{\cdot}CO{\cdot}CH{:}CH{\cdot}C_6H_5$.

On adding 2—3 drops of piperidine to the mixture of phenyl mercaptan (1 gram) and a benzene solution of dibenzylideneacetone (2·2 grams) and leaving the solution for half an hour, and then pouring into it light petroleum, a white solid is precipitated. This product dissolves somewhat readily in boiling alcohol, and, on cooling, crystallises in colourless needles which melt at 121—122°. On analysis, numbers were obtained which indicated that this product is a mixture of the additive compounds of the diolefinic ketone with one and two molecules of the mercaptan. The melting point is raised to 127—128° by a second crystallisation from the same solvent, but, as is indicated by the following analysis, the substance is still impure.

0·2010 gave 0·5864 CO_2 and 0·1061 H_2O. C = 79·56; H = 5·86.
$C_{23}H_{20}OS$ requires C = 80·23; H = 5·81 per cent.

Diphenylthioldibenzylacetone, $[C_6H_5{\cdot}CH(S{\cdot}C_6H_5){\cdot}CH]_2{\cdot}CO$.

This compound, which has been prepared before by Posner (*loc. cit.*), is readily formed on adding piperidine to the benzene solution of equal weights (2 grams) of dibenzylideneacetone and phenyl mercaptan. After a short time, the mixture sets to a semi-solid which dissolves in boiling alcohol with difficulty and, on cooling, crystallises in colourless, iridescent prisms. These, after a second crystallisation from the same solvent, melt at 134—135°, as compared with 139—140° found by Posner, and gradually dissolve in cold concentrated sulphuric acid forming an orange solution which slowly turns red.

0·2003 gave 0·5617 CO_2 and 0·1033 H_2O. C = 76·48; H = 5·72.
$C_{29}H_{26}OS_2$ requires C = 76·65; H = 5·72 per cent.

The Union of Mercaptans with Cinnamylideneacetophenone.

I have studied this reaction with special care in order to examine whether cinnamylideneacetophenone takes up 2 molecules of mercap-

tans, as stated by Posner; but I find that it unites with 1 molecule only of *iso*amyl or phenyl mercaptan and yields compounds which are isomeric with the additive products of dibenzylideneacetone with 1 molecule of these mercaptans.

*Phenyl β-iso*Amylthiol-γ-benzylidenepropyl Ketone*, $C_6H_5 \cdot CH{:}CH \cdot CH(S \cdot C_5H_{11}) \cdot CH_2 \cdot CO \cdot C_6H_5$.

I have carried out two experiments; in the first, a mixture in molecular proportions of cinnamylideneacetophenone (2·2 grams), dissolved in benzene, and *iso*amyl mercaptan (1 gram) was treated with 3 drops of piperidine, and, after several hours, the benzene was evaporated. The residual oil, which solidified on stirring, crystallises from dilute alcohol in colourless needles; these melt at 64° and dissolve in cold concentrated sulphuric acid yielding a deep red solution. The second experiment has been performed in a similar manner except that equal weights (2 grams) of the ketone and the mercaptan have been used, and the solution has been kept overnight before evaporating off the solvent. The substance which is formed, after crystallisation from alcohol, melts at 64°. The identity of the two preparations has been further verified by analysis:

I. 0·2025 gave 0·5792 CO_2 and 0·1404 H_2O. C = 78·00; H = 7·70.
II. 0·2012 ,, 0·5745 CO_2 ,, 0·1405 H_2O. C = 77·87; H = 7·75.
$C_{22}H_{26}OS$ requires C = 78·10; H = 7·69 per cent.,

whilst the additive compound with 2 mols. of the mercaptan,
$C_{27}H_{38}OS_2$, requires C = 73·30; H = 8·60 per cent.

Phenyl β-Phenylthiol-γ-benzylidenepropyl Ketone, $C_6H_5 \cdot CH{:}CH \cdot CH(S \cdot C_6H_5) \cdot CH_2 \cdot CO \cdot C_6H_5$.

On mixing phenyl mercaptan and cinnamylideneacetophenone either in molecular quantities or in the proportion of 1 mol. of the ketone to 2 mols. of the mercaptan, and adding a few drops of piperidine to the solutions of these mixtures in benzene, there is formed in both cases the same compound, which is precipitated by light petroleum. The substance is readily soluble in ether or chloroform, not so readily in cold alcohol, and crystallises in colourless needles from its solution in hot dilute alcohol. Both specimens melt at 103—104°, and their solutions in concentrated sulphuric acid are deep red.

0·2014 gave 0·5928 CO_2 and 0·1063 H_2O. C = 80·27; H = 5·86.
$C_{23}H_{20}OS$ requires C = 80·23; H = 5·81 per cent.

$C_{29}H_{26}OS_2$, the additive compound of the diolefinic ketone with 2 mols. of phenyl mercaptan, which, according to Posner (*loc. cit.*), is formed on using hydrogen chloride as a catalytic agent instead of piperidine, requires C = 76·65 ; H = 5·72 per cent.

Although the close agreement of the melting points indicates that Posner's compound is identical with the one thus obtained, yet I have thought it advisable for direct comparison to prepare a specimen according to Posner's directions. For this purpose, dry hydrogen chloride has been passed into a cold solution in glacial acetic acid of the mixture of cinnamylideneacetophenone (2 grams) and phenyl mercaptan (2·5 grams), when, after a short time, the whole sets to a semi-solid ; the substance crystallises from alcohol in colourless needles which melt at 103° and have other properties, such as the shape of the crystals and the solubility, resembling those of the compound formed under the influence of piperidine. I have, moreover, verified the composition of this specimen by analysis :

0·2008 gave 0·5902 CO_2 and 0·1508 H_2O. C = 80·16 ; H = 5·85.
$C_{23}H_{20}OS$ requires C = 80·23 ; H = 5·81 per cent.

Action of Hydrogen Sulphide on Benzylideneacetylacetone.

On passing hydrogen sulphide into a slightly warm alcoholic solution of benzylideneacetylacetone to which a little sodium ethoxide dissolved in alcohol has been added, a white solid is formed. This is insoluble in alcohol or glacial acetic acid, but readily dissolves in chloroform, and is precipitated from this solution by alcohol. The substance softens at 75—85° and is identical with thiobenzaldehyde.

0·2017 gave 0 5065 CO_2 and 0·0920 H_2O. C = 68·49 ; H = 5·06.
C_7H_6S requires C = 68·85 ; H = 4·91 per cent.

I am engaged in the further investigation of the action of mercaptans on olefinic ketonic compounds in the presence of organic bases, and in the study of the additive products which are thus formed.

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CAMBRIDGE.

VI.—*Hydrolysis of Ammonium Salts.*

By Victor Herbert Veley.

Introductory.

In the ordinary text-books of chemistry it is stated in general terms that aqueous solutions of ammonium salts when boiled become acid with the evolution of a vapour of alkaline reaction. More definite statements are to the effect that, under such conditions, triammonium phosphate loses two-thirds of its ammonia, and is converted into ammonium dihydrogen phosphate; also that an aqueous solution of ammonium oxalate loses ammonia even at $-1°$. Such statements appear to imply that these decompositions are to be classed among heat dissociation phenomena, namely, that ammonium chloride, for example, is decomposed when heated either in the dry state or in aqueous solution, according to the same course of events. The object of the present communication is to show that although the net result is the same in both cases, yet the latter is consequent on hydrolysis, $NH_4Cl + H_2O \rightleftarrows NH_4OH + HCl$ and $NH_4OH = NH_3 + H_2O$, and not on heat dissociation.

Investigations (Walker, *Zeit. physikal. Chem.*, 1889, **4**, 319; Arrhenius, *ibid.*, 1894, **13**, 407; Shields, *Phil. Mag.*, 1893, [v], **35**, 365; van't Hoff, *Chemische Dynamik*, 1898, 121—126) on the hydrolysis of salts, such as the cyanides, acetates, and amides, have shown that three cases are possible: (1) salts formed from a weak base and strong acid, (2) salts from a strong base and weak acid, and (3) salts from a weak base and weak acid. Ammonium salts containing the relatively weak base ammonia would probably be included only in categories I and III. In the former, it has been shown both by inversion and conductivity experiments that the amount of hydrolysis is dependent on the mass of water, namely, the dilution, and the condition of equilibrium is represented by the equation:

$$\frac{C_{\text{(acid)}} \times C_{\text{(base)}}}{C_{\text{(salt)}}} = K \text{ (a constant)} \ldots\ldots\ldots \quad (1).$$

In the latter, the amount of hydrolysis is independent of the dilution, and its equation of equilibrium is

$$\frac{C_{\text{(acid)}} \times C_{\text{(base)}}}{C^2_{\text{(salt)}}} = K \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots \quad (2).$$

It will be shown in the sequel that the hydrolysis of ammonium salts, which results from boiling their aqueous solutions, presents these two cases, namely, that (1) its amount is dependent on the dilution, and (2) is independent of the dilution when beyond a certain limiting value.

There is, further, a third case in which hydrolysis is nil or inappreciable at any degree of dilution.

Experimental.

The method of experiment consisted in boiling 100 c.c. of the several aqueous solutions in round-bottomed, Jena glass flasks of about 500 c.c. capacity fitted with inverted condensers,* according to the ordinary process for determining the proportion of ethereal salts by saponification. The duration of each experiment was one hour, at the expiry of which, the flask was disconnected, its contents rapidly cooled, and the amount of free acid estimated and taken as a measure of the ammonia lost. In most cases the proportion of this free acid was estimated by an ammonia solution of approximately decinormal strength, litmus being used as an indicator; in the case of organic acids, which do not give a sharp definition with litmus, caustic soda solution of the same concentration was substituted for ammonia and phenolphthalein for litmus. Although at the ordinary temperature there did not appear to be any risk of the displacement of ammonia by the caustic soda added, yet it is not pretended that the results obtained are of the same order of accuracy. Such a method seemed, however, to be the only escape from an experimental difficulty.

In the case of the tri- and di-ammonium phosphates, which are alkaline in reaction, the process was reversed, a decinormal solution of hydrochloric acid being substituted for ammonia.

A possible source of error would arise when the acid simultaneously liberated with the ammonia was volatile and might also escape, but, so far as observation went, such escaping acid would recombine with the ammonia, and the salt regenerated would be washed back into the solution by the condensed water. A further source of error might arise from differences in roughness of the glass of different flasks, whereby the evolution of ammonia would be facilitated, but a comparative experiment showed no appreciable difference in ammonia lost when two solutions of ammonium nitrate were heated under the same conditions for the same time, but to one of which half a gram of finely divided silica had been purposely added. The solutions taken for most series of experiments were of 1, 0·5, 0·2, 0·1, and 0·05 normal concentrations respectively; but it will be evident that the method of experiment adopted is restricted on the one hand by the solubility of the salts for concentrated solutions, and on the other by the small

* The condensers used were all of glass with straight internal tubes; a slight error would, doubtless, be caused by the few drops which fell back into the main bulk of the solution after the operation of boiling had been stopped.

absolute amount of ammonia lost from very dilute solutions, whereby the experimental error is very largely increased.

Method of Calculation and Expression of Results.

If P represent the loss of ammonia from the solution and M the amount of ammonia originally combined, then $P10^2/M$ will be the percentage molecular loss; for the purpose of avoiding long decimals, the values have been multiplied by 10, and the numbers thus obtained designated as $K = P10^3/M$. For example, two decinormal solutions of ammonium nitrate (0·8 gram in 100 c.c.) containing 0·17 gram of combined ammonia were placed in two sets of apparatus placed in parallel, and heated for the same period of time, as a comparative experiment. The values for K found were 32·3 and 33·8 or a difference of 3 per cent. approximately, which is within the limit, about 5 per cent., of saponification experiments.

Salts Examined.

The salts examined were the bromide, chloride, nitrate, sulphate, the three orthophosphates, formate, acetate, oxalate, succinate, citrate, ethyl sulphate, benzoate, salicylate, benzene- and naphthalene-α-sulphonates; such a list might be greatly extended, but the foregoing series appeared to be representative and served for the purpose of various comparisons.

The salts of the organic acids, with the exception of the oxalate, were obtained from Kahlbaum; the bromide, chloride, nitrate, sulphate, diphosphate, and oxalate were either fine crystalline specimens at hand, or were recrystallised specially. The chlorate was prepared from the barium salt by precipitation with ammonium sulphate and recrystallising; it contained a trace of chloride. The monophosphate was obtained by the addition of glacial phosphoric acid to concentrated ammonia solution until the solution was distinctly acid, a further quantity of acid was added until no precipitate was produced on the addition of barium chloride to a test portion; the solution was partially evaporated and allowed to crystallise. The triphosphate was obtained by the cautious addition of concentrated ammonia to an aqueous solution of the diphosphate; the salt crystallised out in fine needles, which were dried partially by suction, and finally over sulphuric acid.

No variation was made in the method of procedure except in the case of the oxalate, in which case the experiments were conducted in a dark room on account of the ready decomposition of solutions when exposed to sunlight (Downes and Blunt, *Proc. Roy. Soc.*, 1879, **28**, 209; Richardson, Trans., 1894, **65**, 450). In order to determine

whether the decomposition of aqueous solutions of the salt, as stated above to occur even at $-1°$, is due to the hydrolysis of the salt at that temperature, or to its decomposition as induced by sunlight, two seminormal solutions of the salt were taken, one kept in the dark for 14 hours at the ordinary temperature, the other heated for the same time at 40° in a dark chamber, namely, a bacteriological incubator. There was no appreciable loss of ammonia in either case, thus proving that exposure to sunlight was the determining cause in the above-mentioned observation.

Experimental Results.

In the tables given in the sequel, the molecular concentrations in terms of normality *N* are given in the first, and the found values for *K* in the succeeding columns.

CATEGORY I.

Hydrolysis Nil or Inappreciable.

N.	Bromide. *K.*	Chloride. *K.*	Benzenesulphonate. *K.*
1·0	—	1·3	0·7
0·5	0·017	1·2	2·7
0·2	nil	1·08	3·5
0·1	nil	1·4	4·0
0·05	nil	5·8	3·5

As regards these three salts, it is worthy of note that the three acids combined with the ammonia are those which give the highest value, according to Ostwald (*J. pr. Chem.*, 1884, **29**, 401—402), (1) for the hydrolysis of methyl acetate and (2) for the inversion of cane sugar; thus, the persistence with which the ammonia is retained, serves as a measure of the activity of the acid. This point will be further alluded to in the sequel.

CATEGORY II.

Hydrolysis Dependent on Dilution.

N.	Nitrate. *K.*	Sulphate. *K.*
2·0	5·3	—
1·0	19·0	7·6
0·5	20·0	9·5
0·2	30·8	11·2
0·1	38·9	14·3
0·05	80·5	16·5

In the foregoing salts, the amount of hydrolysis increases progressively with the dilution, and more markedly in the case of the nitrate than in that of the sulphate, the limit of which appears to be reached nearly at the point at which the experimental method becomes impossible. As regards the nitrate, the results of which show irregularity, it is probable that the main reaction of hydrolysis is complicated by the decomposition at the temperature used of the liberated nitric acid ; nitrous acid is formed, which interacts with the ammonia (liberated, but not completely boiled off) to give ammonium nitrite, which is at once decomposed into nitrogen and water.

Category III.

Hydrolysis Independent of Dilution at a Limiting Value.

All the other salts examined come under this, the most common category. For the sake of convenience only, these salts have been divided into inorganic and organic respectively.

Salts of Inorganic Acids.

	Chlorate.	Monophosphate.	Diphosphate.
N.	*K.*	*K.*	*K.*
0·5	15·5	14·5	37·3
0·2	18·7	18·6	42·9
0·1	20·3	22·3	40·0
0·05	18·5	21·5	41·6

The value found for *K* for the triammonium phosphate was 600 approximately, but the salt is relatively unstable, and probably both hydrolysis and dissociation proceed simultaneously.

Salts of Organic Acids.

These salts are further divided for the purpose of convenience into those of (1) paraffinoid and (2) benzenoid acids.

Salts of Paraffinoid Acids.

	Formate.	Acetate.	Oxalate.	Succinate.	Citrate.	Ethyl sulphate.
N.	*K.*	*K.*	*K.*	*K.*	*K.*	*K.*
1·0	37·2	53·4	—	235·6	215·5	4·0
0·5	35·6	95·8	—	230·0	198·6	8·34
0·2	22·0	90·3	17·4	244·6	280·0	10·4
0·1	20·1	94·0	22·3	243·8	275·0	11·1
0·05	19·1	90·3	23·2	240·0	282·0	12·6
0·025	—	100·0	22·8	—	—	—

Salts of Benzenoid Acids.

N.	Benzoate. *K.*	Salicylate. *K.*	Naphthalene-α-sulphonate. *K.*
1·0	3·1	9·8	2·6
0·5	9·0	11·0	9·0
0·2	10·3	14·0	10·0
0·1	10·6	16·0	15·0
0·05	11·1	14·4	14·9

The only point of special notice in the foregoing table is the behaviour of the formate, which differs from all the other ammonium salts examined in that the value for *K* decreases with decrease of concentration. Two series of experiments were conducted, but the values obtained were concordant within the limits of experimental error. Hydrocyanic acid, which might be formed according to the equation $HCO_2NH_4 = HCN + 2H_2O$ (and is thus produced when the dry salt is heated), was tested for, but with a negative result. At present, it is not proposed to offer any explanation of this discrepancy.

Discussion of Results.

In a preceding section, it was observed that the ammonium salts of those acids which give the highest values for the hydrolysis of methyl acetate and of the inversion of cane sugar were those which gave the lowest values in the present investigation.

It appeared worthy of interest to pursue this comparison further, and for this purpose the values for 1/10th molecular concentration have been selected, this being the concentration at which such values have attained constancy. The nitrate and formate are omitted from the present discussion as hydrolysis in both these cases is doubtless modified by secondary reactions. In the following table, the values of *K* for the remaining salts are arranged in order of increasing magnitude in column I, and their reciprocals $1/K$ consequently in order of decreasing magnitude.

Salts.	*K.*	$1/K$.	Chloride = 100.
Bromide	nil	∞	—
Chloride	1·4	0·713	100·0
Benzenesulphonate	4·0	0·250	35·2
Benzoate	10·6	0·094	13·2
Ethyl sulphate	11·0	0·091	11·2
Sulphate	14·0	0·073	10·2
Naphthalene-α-sulphonate	15·0	0·066	9·2
Salicylate	16·0	0·062	8·7
Chlorate	20·3	0·049	6·9
Oxalate	22·3	0·045	6·9
Diphosphate	40·0	0·025	3·5
Acetate	90·0	0·011	1·5
Succinate	243·8	0·004	0·57
Citrate	275·0	0·003	0·51

As a further comparison, the reciprocals $1/K$ have been calculated in terms of the chloride taken as 100 (column III).

In the following table, the acids are arranged in the order of avidity for ammonia in column I, and in column II in their order (mean value) obtained in the investigations of Ostwald (*vide supra*) so far as the comparison may be instituted.

I.	II.	I.	II.
Hydrobromic.	Hydrobromic.	Phosphoric.	Phosphoric.
Benzenesulphonic.*	Benzenesulphonic.	Acetic.	Citric.
Hydrochloric.	Hydrochloric.	Succinic.	Succinic.
Ethyl sulphuric.	Ethyl sulphuric.	Citric.	Acetic.
Sulphuric.	Chloric.		
Chloric. }	Sulphuric.		
Oxalic. }	Oxalic.		

The similarity as regards the relative order of magnitude is very striking; the order of absolute magnitude differs generally as to the high values of the two haloid acids, whereby all the values of most of the remaining acids are consequently reduced, and particularly as to the case of chloric acid, which should rank with the haloid acids, but as a matter of fact comes much below them; but a consequent decomposition of the chloric acid formed in the reaction studied may possibly be a disturbing factor.

This line of investigation might be further extended, not only to the ammonium salts of other acids, but also to the substituted ammonium salts of the same acids. The present communication may serve as a preliminary to further accounts of investigations, although it is not, of course, pretended that the method adopted is of such an order of accuracy as others on the magnitude of chemical change under definite conditions.

I am indebted to Mr. John, of Jesus College, Oxford, for assistance in the earlier portion of this work.

Conclusions.

When aqueous solutions of ammonium salts are heated at their boiling point, the evolution of ammonia and concomitant acidity of solutions result not from a direct dissociation, but from hydrolysis. Three cases are presented: (1) such hydrolysis is nil or inappreciable, (2) it is dependent on the dilution, and (3) it is independent of dilution when beyond a certain limiting value.

The persistence or avidity with which the several acids retain the

* Caldwell, *Proc. Roy. Soc.*, 1904, **74**, 185.

ammonia in combination is analogous to their activity or avidity in the cases of hydrolysis of methyl acetate, and inversion of cane sugar; the relative, but not the absolute, order of magnitude is the same in all these three chemical changes.

VII.—*Studies in Optical Superposition. Part I.*

By Thomas Stewart Patterson and Francis Taylor, B.Sc.

Optical superposition is the somewhat unsuitable term which has been applied to the combination of two or more optically active radicles in one molecule. Such compounds have hitherto received but little systematic investigation, although it seems possible that their examination might lead to interesting results in regard to various phenomena such as those connected with solution or with the combination of radicles generally.

When in a simple active molecule such as that of lactic acid the replaceable hydrogen atoms are substituted by radicles like methyl and ethyl or acetyl and benzoyl, the change in rotation which occurs with each substitution is probably due, not merely to the addition of a new group, but also to a modification, a slight molecular rearrangement, of the active radicle itself. That is, the lactyl radicle, supposing it could be detached from a molecule of methyl lactate without suffering any other change, would show, when examined polarimetrically, a rotation differing from that of a lactyl radicle separated, in the same manner, from a molecule of some other lactate. The inactive group would, of course, be expected to show a similar behaviour; for instance, it is probable that the ethyl radicle in ethyl lactate has not the same volume as in ethyl acetate.

Polarimetric examination of compounds composed of an active and an inactive radicle can scarcely be expected to yield any information as to the changes taking place in both parts of the molecule, but more interesting results may be anticipated from the investigation of compounds formed of two active radicles.

It must be noticed, however, that although in the latter case both parts of the molecule contribute to its rotation, it is not possible to estimate accurately the effect of each. The observed rotation is only a resultant, and for the present a resolution can, at the best, be only very approximately effected by comparison of this resultant rotation with the rotations of substances containing these active radicles united to other inactive groups.

It is proposed in this and some succeeding papers to collect rotation data for such compounds in order to determine as far as possible the mutual influence of the groups of which they are composed, the present communication dealing with menthol and certain of its derivatives.

A sample of menthol which gave for its rotation in absolute alcoholic solution of $c=4\cdot5112$ the value $[\alpha]_D^{19^\circ} -49\cdot88^\circ$ was carefully distilled under diminished pressure and the rotation of the homogeneous substance determined at several different temperatures, with the following results :

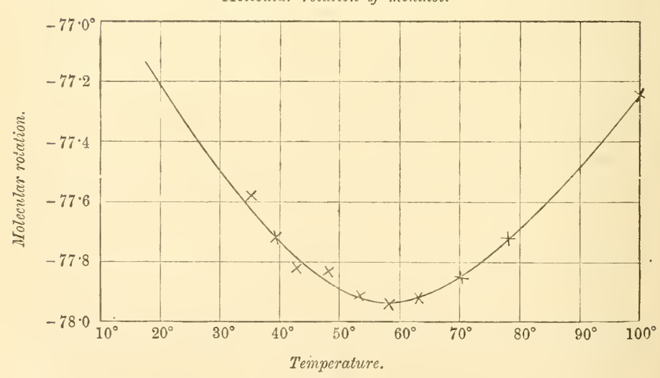
Rotation of Menthol.

t.	$\alpha_D^{t^\circ}$ (66·04 mm.).	Density.	$[\alpha]_D^{t^\circ}$.	$[M]_D^{t^\circ}$.
100·0°	−27·399°	0·8380	−49·51°	−77·24°
78·0	28·132	0·8551	49·82	77·72
70·2	28·380	0·8612	49·90	77·85
63·2	28·585	0·8666	49·95	77·92
58·3	28·720	0·8704	49·96	77·94
53·5	28·833	0·8742	49·94	77·91
48·2	28·937	0·8783	49·89	77·83
43·0	29·055	0·8821	49·88	77·82
39·5	29·118	0·8852	49·82	77·72
35·2	29·177	0·8884	49·73	77·58

Densities Determined :

Temperature	40·9°	59°	80°
Density..................	0·8839	0·8699	0·8534

Molecular rotation of menthol.



From these data, the curve showing the variation of molecular rotation with change of temperature has been drawn. The rotation

of fused menthol has previously been determined by W. H. Perkin (Trans., 1902, **81**, 309), who found $[\alpha]_D^{47°} - 49·88°$, whence $[M]_D^{47°} - 77·82°$, whilst from the foregoing curve the value $[M]_D^{47°} - 77·85°$ is obtained; these numbers agree with one another very closely. It will be noticed at once from this curve that for menthol there exists a temperature of maximum negative rotation. As the temperature falls, the rotation, which at 100° is −77·24°, gradually increases to reach its maximum value of −77·94° at 58—59°. At this temperature, the menthol molecule has its greatest optical effect. A diminution of rotation occurs with further reduction of temperature, but this could only be investigated for a few degrees below the melting point (42°), as the substance did not long remain supercooled. It would appear, however, by extrapolation, that menthol at 20° would have a molecular rotation of about −77·22°, almost the same as at 100°.

Several somewhat similar instances have recently been discovered. Thus it has been shown that, in solutions of optically active compounds, maximum or minimum values of the rotation may be reached at definite concentrations, the temperature being constant, as is the case with nicotine in dilute aqueous solution or camphor in valeric or caproic acid (see Landolt, "Das Optische Drehungsvermögen, Eng. ed., p. 199), and also with ethyl tartrate in various solvents (Patterson, Trans., 1901, **79**, 178, 483; 1902, **81**, 1099). Similarly, maxima or minima may occur at definite temperatures in solutions of certain concentrations, as has been found for solutions of ammonium and sodium molybdenylbimalates (Grossman and Pötter, *Ber.*, 1904, **37**, 84) and for various tartrates (Patterson, Trans., 1904, **85**, 1136).

So far as we are aware, however, only one case strictly analogous with that of menthol has been observed. P. F. Frankland and Wharton (Trans., 1896, **69**, 1587) found that ethyl dibenzoyltartrate exhibits a maximum negative rotation at a temperature close to its melting point, the phenomenon being more pronounced than in the case of menthol, whilst ethyl di-*o*-toluyltartrate, another substance prepared by these authors, very probably has the same peculiarity. In these two cases the phenomenon must be due—since the molecule is symmetrical—to a configuration of maximum asymmetry having been reached. The same explanation may, of course, hold in the case of menthol, but here there is also the possibility that the variation of rotation with change of temperature is merely an indication of the successive preponderance of one or other of the asymmetric carbon atoms. It does not follow that at the temperature of maximum rotation all three are acting in the same sense or with their maximum power.

l-*Menthyl* d-*tartrate* was prepared by Patterson and Dickinson's method (Trans., 1901, **79**, 280). Dry hydrogen chloride was passed

D 2

into a flask containing a mixture of 25 grams of ethyl tartrate (1 mol.) and 120 grams of menthol (4 mols. approximately). This soon caused liquefaction of the menthol, and the resulting solution generally acquired a red colour. The flask was then placed in an oil-bath and the temperature gradually raised to, and kept at, 120—130°, the passage of the hydrogen chloride being continued for about 24 hours. The excess of menthol was then distilled off under reduced pressure and the residue, a heavy yellow or red oil, which forms a resin on cooling, dissolved in a large volume—one to two litres—of warm spirit, to which water was added until a slight turbidity occurred, which was then just removed by alcohol. The substance has a considerable tendency to separate as an oil, but can be obtained without much trouble in the form of silky needles radiating from nuclei. It is generally advisable to dissolve the crystals in alcohol and boil with animal charcoal for an hour or two and then recrystallise several times. The crystals are sticky to the touch and melt at 74—75°. In absolute alcohol ($c = 2$, $l = 200$ mm., $t = 19·5°$) the observed rotation was $-2·843°$, whence $[\alpha]_D^{19·5°} - 71·08°$, and $[M]_D^{19·5°} - 302·4°$.

0·2939 gave 0·7244 CO_2 and 0·2644 H_2O. C = 67·21 ; H = 10·0.
0·2384 ,, 0·5908 CO_2 ,, 0·2120 H_2O. C = 67·59 ; H = 9·88.
$C_{24}H_{42}O_6$ requires C = 67·61 ; H = 9·86 per cent.

Molecular weight determinations carried out in benzene and ethylene bromide gave the following results :

Benzene. Constant = 50.

Substance.	Solvent.	Δ.	M. W.
0·1596	11·045	0·161	448·7
0·2698	10·964	0·276	445·8
0·3850	10·833	0·391	452·5

Ethylene Bromide. Constant = 118.

0·1663	28·669	0·149	459·4
0·3766	28·669	0·349	444·1

$C_{24}H_{42}O_6$ requires M. W. = 426·0

These numbers show evidence of only slight association, and together with the analyses leave no doubt as to the identity of the substance. Further proof is, however, furnished by the fact that a specimen of the compound obtained from methyl tartrate instead of from the ethyl ester was found to be identical in melting point and rotation with the foregoing preparation, thus conclusively proving the presence in the molecule of two menthyl groups.

In order to ascertain whether the process of preparation had in any

way affected the rotation of the menthol used, a small quantity of the ester was decomposed by boiling with dilute caustic soda solution, and the menthol obtained, after shaking with water and caustic soda solution, dried, and distilled under diminished pressure. When dissolved in absolute alcohol and examined in the polarimeter, it gave for $c=4\cdot5112$, $[\alpha]_D^{18°}$ $-49\cdot21°$. The original value for the same concentration was $[\alpha]_D^{19°}$ $-49\cdot88°$; the slight difference between these numbers was doubtless due to imperfect purification of the small quantity of menthol recovered.

The rotation of this menthyl tartrate was then determined, and on account of the fact that it remains supercooled for a long time the observations could be extended far below the melting point.

Rotation of l-*Menthyl* d-*Tartrate.*

t.	$\alpha_D^{t°}$ (40 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
100°	−24·61°	0·9920	−62·02°	−264·2°
75	25·60	1·0117	63·26	269·5
67·5	26·05	1·0176	64·00	272·6
61·7	26·27	1·0220	64·26	273·7
57·2	26·49	1·0255	64·58	275·1
50·1	26·84	1·0312	65·08	277·2
39·3	27·25	1·0397	65·52	279·1
20·7	28·09	1·0540	66·63	283·9
8·5	28·58	1·0636	67·18	286·2
5·5	28·75	1·0660	67·42	287·2

Densities Determined:

Temperature...... ...	80°	100°	134·8°	163°
Density..	1·0110	0·9920	0·9654	0·9436

As has already been mentioned, an idea of the effect of each of the two active radicles in a compound such as the above can only be obtained from analogy with the behaviour of other, simpler substances. The figures in the table must therefore be compared with the rotation data of compounds of tartaric acid with inactive radicles on the one hand and of menthol with inactive radicles on the other.

The behaviour of a few tartaric esters as regards variation of rotation with change of temperature is known fairly completely (compare Trans., 1904, **85**, 766), but although a considerable number of menthyl esters have been prepared, notably by Tschugaeff (*Ber.*, 1898, **31**, 364), the influence of temperature change on their rotations does not appear to have been investigated. In order, therefore, to obtain some information on this point, a specimen of menthyl acetate was prepared from menthol and acetyl chloride and distilled several times *in vacuo*, the last distillation being performed with a Hempel tube.

The boiling point of the specimen used was very steady at 116°

(bath, 182—185°; 22 mm. pressure). The substance was examined in the polarimeter with the following results:

Rotation of l-*Menthyl Acetate.*

t.	$\alpha_D^{t°}$ (40 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
13·0°	−29·637°	0·9307	−79·61°	−157·6°
16·6	29·488	0·9278	79·46	157·3
36·9	28·848	0·9115	79·12	156·7
53·0	28·408	0·8981	79·08	156·6
67·1	27·963	0·8865	78·86	156·1
98·1	27·071	0·8612	78·59	155·6

Densities Determined:

Temperature	15°	26·2°	46·8°	80·45°
Density	0·9292	0·9201	0·9034	0·8756

From these numbers, the value −157·35° is found for the molecular rotation at 20°, whilst Tschugaeff (*loc. cit.*) gives −157·25°. Although these values agree very well, it may be noted that our number for observed rotation, −73·5° ($t = 20°, l = 100$), is somewhat higher than his (−72·95°), and this is also the case with the density. We find $d 20°/4° = 0·9251$, whilst Tschugaeff gives $d 20°/4° = 0·9185$. We have determined the density of two quite different preparations with the same result in each case.

The rotation of *l*-menthyl acetate is but little influenced by change of temperature, and it is affected in the same manner as is the rotation of the tartaric esters. By extrapolation from the data given in the table, the value −157·9° is obtained for the molecular rotation at 0° and −155·6° at 100°.

If now the numbers for menthyl acetate and menthyl tartrate are compared with those for menthol itself, it will be noticed in the first place that the maximum negative rotation observed in the case of the last named is not apparent in either of the esters.

Menthol suffers very little alteration of rotation with variation of temperature. Between 60° and 100°, the molecular rotation only changes by 0·7°. The change of rotation of the acetate is also but slight, namely, −2·3° between 0° and 100°. In the case of the tartrate, however, the change is much greater, namely, 23·5° (from −288° at 0° to −264·5° at 100°), and, arguing from analogy, the part of this variation due to the two menthyl groups should be about twice as great as in the acetate, 4·6°, so that the remaining 18·9° would be due to the tartaryl radicle, a value which agrees as closely as could be expected with those for the same changes in methyl, ethyl, and *n*-propyl tartrates, namely, 11°, 16·9°, and 15·85° (Trans., 1904, **85**, 768).

As regards the absolute value of the rotations, it may be noticed that the substitution of an acetyl group for the hydrogen atom of the hydroxyl group in menthol lowers the rotation very considerably—from $-77 \cdot 22°$ to $-157 \cdot 35°$ at 20°. Now it has been found by Tschugaeff (*Ber.*, 1898, **31**, 364) that the substitution of other homologous groups in place of acetyl in menthyl acetate is practically without effect on the molecular rotation of the resulting compounds. But, as has just been shown, the molecular rotation of menthyl tartrate at 20° is $-284°$, and is due partly to the two menthyl residues and partly to the tartaryl radicle joining them. These two components will be opposed to each other, since tartaric esters containing inactive alkyl groups have at 20°, so far as is known, positive rotations. The rotatory effect due to the two menthyl groups in menthyl tartrate must therefore be greater than $-284°$, and must thus have a value approximating to twice the rotation of menthyl acetate. This would seem to indicate that, in spite of the considerable difference of composition, the group –CO·CH(OH)–, consisting of half the tartaryl radicle, has, when substituted for the hydroxylic hydrogen of menthol, an optical value much the same as that which is common to acetyl, *n*-propyl, and *n*-butyl.

l-*Menthyl Diacetyl*-d-*tartrate*.

This substance was prepared by heating menthyl tartrate with excess of acetyl chloride for 2 to 3 hours. The undecomposed acetyl chloride was then distilled off and the viscid residue shaken with dilute sodium carbonate solution and then with water. After being recrystallised several times from dilute alcohol, the ester melted at 84·5°.

We had occasion at a later period to make another preparation of this compound, and the crystallisation was started by sowing in a few particles of the original specimen. The melting point of the product was found, however, to be 108°. The melting point of the first sample—which had been left in a stoppered bottle for some months—was then redetermined and found to be also 108°. The rotation had nevertheless remained unaltered.

In order to verify these observations, a third specimen of the acetyl derivative was made, using freshly-prepared menthyl tartrate. After the acetyl chloride had been distilled off, the crude product was treated as in the first case. The solid obtained melted at 84°. A little of this substance was then melted on a spatula and allowed to cool, and a few small crystals of the preparation melting at 108° mixed with it. The glassy substance obtained was powdered on porous plate. On heating, it appeared to soften at about 50°, and then, as the temperature rose, it became opaque again and finally melted at 106—108°.

l-Menthyl diacetyl-*d*-tartrate therefore exists in two crystalline forms, as is also the case with methyl tartrate (Trans., 1904, **85**, 765).

The original preparation in absolute alcoholic solution of $c=2$ gave a rotation of $-2.04°$ in a 200 mm. tube at 15°, whence $[\alpha]_D^{15°} -51.0°$ and $[M]_D^{15°} -260.1°$.

0·2608 gave 0·6259 CO_2 and 0·2079 H_2O. C = 65·45; H = 8·86.
0·2467 „ 0·5927 CO_2 „ 0·1981 H_2O. C = 65·52; H = 8·92.
$C_{28}H_{46}O_8$ requires C = 65·88; H = 9·02 per cent.

The composition of this substance was further verified by preparation and analysis of the chloroacetyl derivative of menthyl tartrate (see p. 42) and by the following molecular weight determinations:

Solvent: *Benzene*. Constant = 50. M. W. = 510.

Substance.	Solvent.	Concentration.	Δ.	M. W.
0·0414	7·537	0·549	0·054	508·5
0·3488	7·537	4·63	0·487	475·2
0·6213	6·805	9·00	1·014	455·0
0·9137	7·798	11·72	1·347	435·0
1·0127	6·805	14·88	1·755	424·0
1·3666	7·798	17·52	2·117	414·0

According to these numbers, the molecular weight diminishes with increasing concentration, which may perhaps be due to combination of solvent and solute. Somewhat similar cases have been observed by Kahlenberg and Lincoln (*Jour. Physical Chem.*, 1899, **3**, 19; *Chem. Centr.*, 1899, i, 810) and Walker (Trans., 1904, **85**, 1110).

Polarimetric examination of the ester gave the following numbers:

Rotation of l-*Menthyl Diacetyl*-d-*tartrate.*

t.	$\alpha_D^{t°}$ (40 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
99·2°	−17·720°	0·9915	−44·68°	−227·8°
73·2	18·700	1·0100	46·29	236·1
68·9	18·873	1·0130	46·57	237·5
62·1	19·102	1·0180	46·91	239·2
59·9	19·337	1·0195	47·42	241·8
46·3	19·870	1·0292	48·27	246·2
39·3	20·198	1·0342	48·83	249·0
26·6	20·755	1·0434	49·73	253·6
14·4	21·363	1·0522	50·76	258·9
20·0	—	—	50·28 *	256·4 *

Densities determined:

Temperature................	115°	158·5°
Density...	0·9804	0·9494

* Interpolated.

With regard to these numbers, little can be said, inasmuch as other data with which they might be compared are scarce. Ethyl diacetyltartrate appears to be the only diacetyl ester the rotation of which has been investigated as regards temperature change, and it, in its optical behaviour, seems in most points to be related to ethyl tartrate in just the opposite way to that in which menthyl diacetyltartrate is related to menthyl tartrate.

Thus the molecular rotation of ethyl tartrate is greater at temperatures between 0° and 100° than that of the diacetyl derivative. It might therefore be expected that the diacetyl-menthyl compound would have a greater negative rotation than menthyl tartrate, which is not the case. Again, the temperature-coefficient of ethyl diacetyltartrate is less than that of ethyl tartrate, whilst for the menthyl esters the opposite holds.

Some explanation of this may be obtained, however, from the following table, in which such data as are available regarding the influence of the substitution of acetyl groups are collected :

	Simple Tartaric Esters.	*Diacetyl Derivatives.*
Methyl......	$[M]_D^{20°}$ +3·68°.*	$[M]_D^{18°}$ −37·28° † (in alcohol $c = 3·566$).
Ethyl	$[M]_D^{20°}$ +15·95°.*	$[M]_D^{20°}$ +9·9°.‡
n-Propyl ...	$[M]_D^{20°}$ +29·67°.*	$[M]_D^{20°}$ +42·93°.§
n-Butyl ...	$[M]_D^{20°}$	$[M]_D^{20°}$ +61·59°.‖

It will be observed that, although in the methyl esters the rotation of the acetyl derivative is much lower than that of the simple ester, the difference in the case of the ethyl esters is considerably less, whilst in the propyl compounds the acetyl derivative has the greater rotation. Unfortunately, although Freundler has examined the rotation of *n*-butyl diacetyltartrate, he has not recorded the rotation of the simple ester, and therefore this point can only be imperfectly discussed. It appears, however, that as the alkyl radicle increases in weight the difference between the rotations of corresponding substances diminishes, and finally the rotation of the acetyl compound becomes greater than that of the parent ester, and since the menthyl radicle is of considerable size it would naturally be expected to resemble the propyl group rather than the methyl group.

As there is not much difference between the analytical numbers for the mono- and di-acetyl derivatives of menthyl tartrate, l-*menthyl di-*

* Patterson, Trans., 1904, **85**, 766. † Pictet, *Jahresber.*, 1882, 856.

‡ Patterson and McCrae, Trans., 1900, **77**, 1098.

§ *Compt. rend.*, 1893, **117**, 556. ‖ Freundler, *Compt. rend.*, 1892, **115**, 509.

monochloroacetyl-d-*tartrate* was prepared with the object of verifying the composition of the acetyl derivative. It has been shown (Frankland and Patterson, Trans., 1898, **73**, 185) that whereas two acyl groups can be introduced into the methyl and ethyl tartrate molecules by the action of mono- and di-chloroacetyl chlorides, only one acyl group is introduced by trichloroacetylchloride. It is probable, therefore, that chloroacetyl chloride acts less readily than acetyl chloride, so that if the former yields a diacyl derivative (which can, of course, be very definitely determined by a chlorine estimation) the latter must yield a diacyl compound also.

The substance obtained by the action of chloroacetyl chloride on *l*-menthyl *d*-tartrate was crystallised several times from methyl alcohol. It melted, rather indefinitely, at 99—102°.

0·2310 gave 0·1142 AgCl. Cl = 12·23.
$C_{28}H_{44}O_8Cl_2$ requires Cl = 12·25 per cent.

Polarimetric examination of the compound in absolute alcoholic solution gave the following results: $c = 1$; $l = 200$ mm.; $t = 19°$, observed rotation = $-0·85°$, whence $[\alpha]_D^{19°} - 42·5°$ and $[M]_D^{19°} - 246·1°$.

This investigation is at present being extended in other directions. The results so far obtained may be summarised as follows:

(1) Menthyl acetate, menthyl tartrate, and menthyl diacetyltartrate have been prepared, and their rotations examined between 0° and 100° and compared with each other and with that of menthol between the same temperatures.

(2) Menthyl diacetyltartrate is dimorphous, one modification melting at 84·5° and the other at 108°.

(3) It has been found that for menthol there is a temperature (58—59°) of minimum rotation (maximum negative rotation), but no such temperature has been observed for its derivatives.

(4) It seems possible, reasoning by analogy, to trace the separate effects of the different active groups composing menthyl tartrate and its diacetyl derivative.

In conclusion, the authors desire to acknowledge their indebtedness for grants from the Government Fund of the Royal Society and from the Chemical Society Research Fund, which defrayed the expenses of this investigation.

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The University, Leeds.

VIII.—*The Available Plant Food in Soils.*

By Herbert Ingle.

Considerable attention has recently been devoted by agricultural chemists to the methods by which some knowledge of the amounts of the mineral constituents of plant food present in soil in a condition available to plants might be acquired. It has long been recognised that estimations of the total quantities of phosphoric acid, potash, and lime present in a soil are of little value as indications of its fertility or of its manurial requirements.

In a recent paper by Hall and Plymen (Trans., 1902, **81**, 117), a review of the various methods proposed for the estimation of the available phosphoric acid and potash is given, as is also a comparison of the results obtained by these methods, with the known manurial needs of several soils as indicated by field trials. These authors find that amounts of phosphoric acid and potash extracted by treatment of soils with dilute acids are much more closely proportional to the quantities present in an available condition than those obtained by the use of strong hydrochloric acid. They at the same time assert that no sharp line of distinction can be drawn between the available and non-available phosphates and potash, and that every method tried gave empirical results. They finally conclude that of all the methods used :—(1) extraction with a 1 per cent. solution of citric acid, (2) with equivalent quantities of hydrochloric acid and acetic acid, (3) with a saturated solution of carbonic acid, and (4) with an ammoniacal solution of ammonium citrate, the first named gave results most in agreement with the actual relative fertility of the soils.

This particular strength of citric acid solution was apparently first suggested by Stutzer (*Chem. Centr.*, 1884, **5**, 329; Abstr., 1885, **48**, 439) as a solvent for extracting the "available" phosphates from manures, instead of the usual ammonium citrate solution. The method, the value of which as applied to manures was confirmed by Thomson (Abstr., 1886, **50**, 392), was recommended by Dyer (Trans., 1894, **65**, 115) for estimating the available mineral plant food in soils. Dyer was led to use a 1 per cent. solution of citric acid from the results of the determinations of the average sap acidity of the roots of a large number of plants. He showed by an application of the method to the barley soils of the Hoos Field, Rothamsted, that its indications were endorsed by the results of actual field trials. Subsequent experience has confirmed the value of the process, which is now largely used in soil analysis under the name of "Dyer's method."

It occurred to the writer that the growth of plants in soil from

which the available phosphoric acid and potash had been extracted by Dyer's method might afford useful information. So far as he can ascertain, no experiments on these lines have been made.*

Preparation of the Soil.

About three hundredweights of soil from an arable field at the Garforth Experimental Farm were taken in February, 1901, to a depth of six inches and sent to the laboratory by rail. The soil was air-dried on a clean concrete floor for about a week with occasional stirring. It was then sifted through a sieve with quarter-inch square meshes and the fine portion preserved in a cask. This air-dried soil lost 11·6 per cent. of moisture when heated in the steam oven.

A portion of the soil was extracted with a 1 per cent. solution of citric acid, exactly as in Dyer's method. The extraction was performed in a large tin cylinder provided with a finely perforated double false bottom; between the two metal plates, a piece of fine linen cloth was placed and, by means of a filter pump attached to a tubulure in the cylinder below the false bottom, the extract could be filtered off. Filter paper was first tried, but the cloth was found to be much more serviceable. The cylinder was fitted with a rotatory wooden stirrer driven by a water motor.

By means of this apparatus, ten kilograms of soil could be treated with a hundred litres of citric acid solution at a time. Allowance was made for the water contained in the air-dried soil. At each extraction, the stirrer was kept running night and day for seven days, and periodically a quantity of the liquid from below was drawn off and added at the top so as to maintain the uniformity of the concentration of the liquid. After each extraction, the clear liquid was removed from below by means of the filter pump, an operation which took about two days, and the soil washed five or six times with distilled water. The soil was then drained as thoroughly as possible by suction, removed from the apparatus, and dried. By repeating this operation four times, about thirty-three kilograms of dried, extracted soil were obtained. This was well mixed together in order to secure uniformity, and used in the pot cultures. The soil was taken from the field and

* Since this account was written, a paper by Söderbaum has appeared (*Kungl. Landtbruks-Akademiens handlingar och tidskrift,* 1903, 103—106; *Bied. Centr.*, 1903, **32**, 795—798), describing the results obtained by growing barley in soils which had previously been extracted for forty-eight hours with a 2 per cent. solution of hydrochloric acid at the ordinary temperature. The results show that such soil is incapable of supporting plant life, but that the addition of calcium carbonate in a great measure restores its fertility. Neither analyses of the soil or crops nor determinations of the amounts of phosphoric acid and potash removed by the acid treatment are given in this paper.

the extraction made in the early spring of 1901 and the plants were grown in the same year, but the pot cultures were repeated with more care in 1902.

The original soil was analysed with the following result:

	Per cent.		Per cent.
Stones removed by 3 mm. sieve	2·27	Ferric oxide and alumina	6·64
		Lime	0·81
The fine soil contained:		Magnesia	0·31
Moisture	3·77	Phosphorus pentoxide	0·16
Loss on ignition	6·63	Potash	0·14
(containing nitrogen, 0·259 per cent.).		Not determined	1·24
Silica and insoluble matter	80·30		100·00

On treating the soil for seven days with a 1 per cent. solution of citric acid, the following constituents were extracted:

	Per cent.		Per cent.
Potash	0·0110	Lime	0·553
Phosphoric oxide	0·062	Nitrogen	0·011

The soil which had been extracted with citric acid was lighter in colour and somewhat more coherent than the original soil.

In order to lessen any influence on the plants due to change in the physical properties of the soil by extraction, both the extracted and the original soils were mixed with ten per cent. of their weight of coarse silver sand, which was freed from any contained plant food by previous treatment with strong hydrochloric acid and thorough washing with water. The new flower-pots employed, which were six inches in diameter, were extracted before use for at least an hour with hydrochloric acid (one of strong acid to four of water) and thoroughly washed. The broken earthenware used for "drainage" at the bottoms of the pots was subjected to the same treatment and one hundred grams were used in each pot.

The Experiments of 1901.

These investigations were vitiated by the very hot weather, the attacks of insect pests, and, in the case of barley, by the depredations of sparrows. They are briefly described because, although the examination of the crops was not completed, the qualitative results may be of some interest.

The three plants selected for experiment were: (1) Barley (Garton's "Standwell"); (2) Turnip ("Tweedale Green Globe"); (3) Horse Bean (variety not ascertained).

Eight pots were assigned to each crop, numbers 1 to 8 to barley, 1*a* to 8*a* to turnips, and 1*b* to 8*b* to beans.

The soil allotted to each pot is shown in the following table:

Pot.	Soil.
1, 1*a*, and 1*b* ...	Original soil.
2, 2*a*, ,, 2*b* ...	Water-washed soil.
3, 3*a*, ,, 3*b* ...	Extracted soil + lime, phosphate, and potash.
4, 4*a*, ,, 4*b* ...	Extracted soil + lime and potash.
5, 5*a*, ,, 5*b* ...	Extracted soil + lime and phosphate.
6, 6*a*, ,, 6*b* ...	Extracted soil only.
7, 7*a*, ,, 7*b* ...	Extracted soil + lime.
8, 8*a*, ,, 8*b* ...	Extracted soil + potash and phosphate.

The lime, potash, or phosphoric acid restored to the extracted soil in certain of the pots was equal to that removed from the original soil by the citric acid treatment. The lime was added in the form of precipitated calcium carbonate, the potash as potassium nitrate, and the phosphoric acid as sodium phosphate. The two latter were added in aqueous solution, whilst the calcium carbonate was well mixed with the soil. The soils were moistened from below with distilled water, and on June 4th were seeded.

Seedlings were visible in all the barley and turnip pots by the 10th of this month, but the beans were not all up before the 18th.

The barley and turnip seedlings in the extracted soil (pots 6 and 6*a*) were very feeble from the first, and the turnips in 6*a* were dead on the 22nd. Additional seeds were sown in this pot on the 19th, and as it was thought that the death of those first sown might be due to lack of nitrates, about 0·15 gram of sodium nitrate was applied in solution to the surface soil in this pot.

In the case of the turnips, and to a less extent with the barley, the signs of starvation soon showed themselves in the extracted soil (pots 6 and 6*a*), as did also the advantages of a liberal supply of plant food (greatest and most readily available being in pots 3 and 3*a*). With beans, these differences were not so apparent in the early stages of growth, although they became so later.

Unfortunately, the turnips, and to a less extent the beans, suffered so much from the attacks of aphides, and the barley was so damaged by sparrows, that it was deemed inadvisable to expend the time and labour necessary for their analysis.

With beans, the following are the weights of the air-dried plants (without roots) at the end of their growth;

Pot.	Weight in grams.	Pot.	Weight in grams.
1*b*	5·305	5*b*	20·441
2*b*	12·385	6*b*	1·047
3*b*	26·385	7*b*	1·454
4*b*	not recorded	8*b*	17·975

With barley, less differences were shown, except with pot 6, the dry weight of the whole plants in this pot being about one-seventh of that of the others.

Summary of the 1901 *Experiments.*

The following general conclusions may be drawn:

(1) In soil treated for seven days with ten times its weight of a 1 per cent. solution of citric acid, the growth of plants is greatly hindered, especially at first, and the total produce is very small.

(2) The restoration of an amount of potash and phosphoric acid, in soluble form, equal to that removed by the citric acid treatment enables the extracted soil to yield a larger crop than could be obtained from the original soil. In other words, the restored plant food is more "available" than that originally present.

(3) Extraction with a 1 per cent. solution of citric acid for seven days does remove from a soil at least the greater portion of the "available" potash and phosphoric acid. In this connection, it must be borne in mind that the available mineral plant food in a soil is being continually renewed by processes of weathering, and that even if its quantity were absolutely *nil* at the commencement of the experiment, it would not remain so, but would increase by the action of moisture and air on the mineral matter.

Another weakness of the method is also realised, namely, that the bacteriological condition of the soil may be affected by the treatment, and this may have an effect on the growth of the plants. How far the results are affected by this influence, the writer is unable to say.

The Experiments of 1902.

In 1901, the plants had to be grown at Garforth, at some distance from the laboratory, and considerable difficulty was experienced in properly attending to them. In 1902, advantage was taken of the offer of one of the writer's students, Mr. W. H. Dobson, to undertake the personal supervision of the growth of the plants at Stapleton Park Gardens, near Pontefract. Mr. Dobson, who is an experienced horticulturist, took the greatest care of the plants, and when he returned them at the end of their growth they were in perfect condition, not a leaf being deranged on any of them.

In this investigation, parallel growths of barley and beans were made in the original soil and in the citric acid extracted soil. In each case, the soil was mixed with 10 per cent. of its weight of white sand which had been thoroughly extracted with hydrochloric acid, as in the previous year's experiments. The pots used and the earthenware employed for "drainage" were also treated with acid and well washed.

Eight pots were used, four for barley and four for beans. Pots 1, 2, 5, and 6 contained the original soil to which 10 per cent. of washed sand had been added; pots 3, 4, 7, and 8 held a mixture of the citric acid extracted soil with 10 per cent. of sand.

Each pot held 1475 grams of the mixture of soil and sand. As it was thought that the extraction and washing of the soil might affect the early growth of the plants by the removal of nitrates, the contents of all the pots were moistened with distilled water containing 10 grains of ammonium nitrate to the gallon (0·143 gram per litre).

On May 2nd, when the soil was thought to be in a suitable condition as to moisture, barley was planted in pots 1, 2, 3, and 4. The next day, beans were planted in pots 5, 6, 7, and 8. The plants were subsequently watered as required with distilled water.

From notes taken by Mr. Dobson, the following are the chief points observed with respect to the growth of the plants:—1. With the comparatively small seeds of barley, the appearance of the seedlings above the ground was considerably retarded in the extracted soil, the dates at which the young plants were first visible in the various pots being:

May 9th	in Pot	No.	1,	that is,	7	days	after sowing.
May 10th	,,	,,	2,	,,	8	,,	,,
May 14th	,,	,,	3,	,,	12	,,	,,
May 15th	,,	,,	4,	,,	13	,,	,,

In the case of the beans, with their larger seeds, no such effect was noted, seedlings appearing on May 22nd in Pots 5 and 8 and on May 23rd in Pots 6 and 7. This is doubtless due to the growth of the barley being more dependent on an early supply of nutriment from the soil than that of the beans, the larger seeds of which supply nourishment to the young plant for a longer period.

2. With both barley and beans, the inferiority of the plants in the extracted soil was greatest during the early periods of growth and became less marked in the later stages, probably because the changes in the extracted soil would gradually render available some of the

mineral matter originally present in an unavailable condition. The following table gives the average height of the barley plants in each pot at the various dates:

Date.	Pot 1.	Pot 2.	Pot 3.	Pot 4.
	Average height in inches.			
June 20th	5·8	4·9	2·8	3·3
July 4th...............	12·8	10·6	4·5	8·1
July 18th	16·2	18·3	9·6	10·0
August 1st...........	20·0	21·0	13·2	14·9
August 15th	20·0	21·0	17·0	15·5

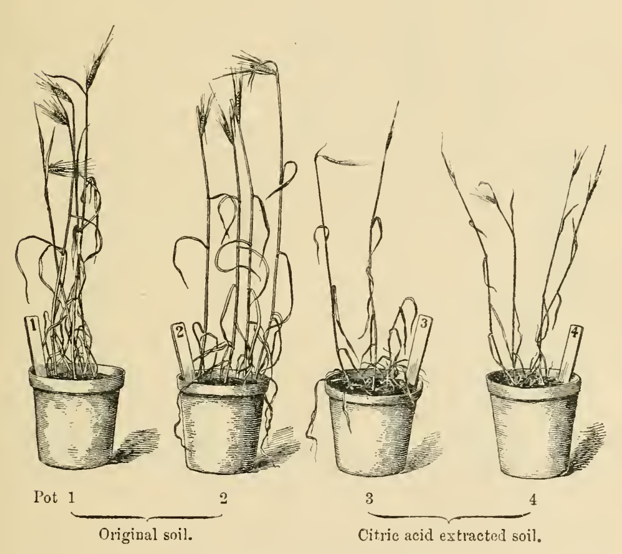


PLATE I.—*Barley*, 1902 *experiment*.

With the beans, the relative progress may be gathered from the following table, giving the height in inches of each plant at the various dates :

Date.	Pot 5. *a.*	Pot 5. *b.*	Pot 5. Mean.	Pot 6. *a.*	Pot 6. *b.*	Pot 6. Mean.	Pot 7. *a.*	Pot 7. *b.*	Pot 7. Mean.	Pot 8. *a.*	Pot 8. *b.*	Pot 8. Mean.
June 6th.........	1·5	2·3	1·9	1·5	2·0	1·8	1·0	1·3	1·2	2·5	1·5	2·0
June 20th	9·0	—	9·0	7·0	6·5	6·8	4·5	3·0	3·8	6·0	5·0	5·5
July 4th	19·3	5·0	12·1	18·3	17·0	16·6	7·8	4·8	6·3	11·0	9·5	10·3
August 15th ...	37·0	16·0	26·5	30·0	30·0	30·0	17·0	17·0	17·0	21·0	16·0	18·5

It is to be noted that in Pot 3 (barley in extracted soil) two of the four plants became very sickly about the end of July, and were dead on August 1st, and that one bean of the two in Pot



PLATE II.—*Beans*, 1902 *experiment.*

5 became "blind" in June, but put out lateral shoots and afterwards grew vigorously.

The plants were photographed on October 8th, by which date they had completed their growth and ripened their seed. They were kept in the laboratory until November 17th, when they were cut off at the surface of the soil and preserved for analysis.

Analysis of the Plants.

The following determinations were made in the yield from each pot:

Weight of the whole air-dried plants.
,, seed.
,, straw.
,, dry matter in straw.
,, ash in straw.

Weight of silica in straw.
,, phosphoric acid in straw.
,, potash in straw.
,, phosphoric acid in seed.
,, potash in seed.

The determinations of silica are not very accurate, inasmuch as some of the lower leaves and straw, especially in the case of beans, were contaminated with particles of soil which it was difficult to remove entirely. The chief interest, however, attaches to the amounts of potash and phosphoric acid contained in the plants.

In the following tables are given the data for each pot, the mean amounts for the two pots containing original soil and for the two containing the extracted soil, and also the ratio of these means.

Barley, 1902.

	Original soil.			Extracted soil.			Ratio
	Pot 1.	Pot 2.	Mean.	Pot 3.	Pot 4.	Mean.	of means.
Weight of whole crop.	4·9060	5·3382	5·1221	1·9000	2·1250	2·0125	2·55 : 1
,, straw	2·6276	2·9030	2·7653	1·2228	1·2104	1·2166	2·27 : 1
,, grain	2·2784	2·4352	2·3568	0·6772	0·9146	0·7959	2·95 : 1
Number of grains......	54	72	63	23	30	27	2·32 : 1
Average weight of one grain	0·0420	0·0324	0·0372	0·0291	0·0305	0·0298	1·25 : 1
In the whole plant:							
Phosphoric acid	0·0206	0·0167	0·0187	0·0040	0·0051	0·0045	4·15 : 1
Potash	0·0702	0·0662	0·0682	0·0188	?	—	3·60 : 1
In the straw:							
Phosphoric acid	0·0040	0·0020	0·0030	0·0012	0·0018	0·0015	2·00 : 1
Potash	0·0548	0·0472	0·0510	0·0172	0·0267	0·0219	2·35 : 1
Silica	0·1072	0·1163	0·1138	0·1200	0·1046	0·1123	1·00 : 1
Total dry matter	2·3263	2·5636	2·4449	1·1073	1·1808	1·1440	2·15 : 1
Ash.......................	0·2472	0·2345	0·2408	0·1780	0·1678	0·1729	1·40 : 1
In the grain:							
Phosphoric acid	0·0166	0·0147	0·0157	0·0028	0·0033	0·0031	4·75 : 1
Potash	0·0154	0·0197	0·0172	0·0016	?	—	11·0 : 1

The weight of the barley grains used as seed in each pot was on the average 0·0528, the total weight therefore of 4 seeds would be 0·2112 gram. The phosphoric acid contained in the 4 grains would amount to 0·00065, the potash to 0·00009 gram.

Beans, 1902.

	Original soil.			Extracted soil.			Ratio
	Pot 5.	Pot 6.	Mean.	Pot 7.	Pot 8.	Mean.	of means.
Weight of whole crop.	14·2802	11·3890	12·8346	2·4444	2·7122	2·5783	5·0 : 1
,, straw	8·3312	7·3875	7·8594	1·7924	2·2522	2·0223	3·9 : 1
,, seed	5·9490	4·0015	4·9752	0·6520	0·4600	0·5560	8·9 : 1
Number of seeds	9	7	8	2	2	2	4·0 : 1
Average weight of one seed	0·6610	0·5736	0·6163	0·3260	0·2300	0·2780	2·2 : 1
In the whole plant:							
Phosphoric acid	0·0341	0·0171	0·0256	0·0100	0·0089	0·0094	2·7 : 1
Potash	0·1297	0·0848	0·1073	0·0465	0·0568	0·0516	2·1 : 1
In the straw:							
Phosphoric acid	0·0130	0·0082	0·0106	0·0042	0·0053	0·0047	2·2 : 1
Potash	0·0928	0·0495	0·0711	0·0424	0·0545	0·0484	1·5 : 1
Silica	0·0537	0·0750	0·0643	0·0474	0·0146	0·0310	2·1 : 1
Total dry matter	7·1700	6·2662	6·7181	1·5622	1·9432	1·7527	3·9 : 1
Ash..................	0·8538	0·7184	0·7861	0·1820	0·1770	0·1795	4·4 : 1
In the seed:							
Phosphoric acid	0·0211	0·0089	0·0150	0·0058	0·0036	0·0047	3·2 : 1
Potash	0·0369	0·0353	0·0361	0·0041	0·0023	0·0032	11·3 : 1

The following are the most important points indicated in the foregoing tables:

1. *Weight of the Whole Air-dried Crop.*

This was, in every case, much greater in the pots containing the original soil. With barley, the total produce of Pots 1 and 2 amounted to 10·2442 grams, that of the two pots containing the extracted soil to 4·0250 grams, these numbers being in the ratio of 2·55 to 1.

In the case of beans, the difference was greater; the two pots of original soil yielded a total crop of 25·6692 grams, whilst the two pots of extracted soil only gave 5·1566 grams, these numbers being in the ratio of nearly 5 to 1.

2. *Weight of the Seed.*

The barley, 126 seeds, from the two pots of original soil weighed 4·7136 grams, that from the two pots of extracted soil, 53 seeds, 1·5918 grams, these numbers being in the ratio of 2·95 to 1. With beans, the difference in yield was greater, the aggregate weights being 9·9505 from the original and 1·1120 from the extracted soil, a ratio of 8·9 to 1.

The seeds produced in the original soil were not only numerically

greater—barley, 126 against 53, beans, 16 against 4—but the average weight of the individual seeds was much greater, especially in the case of the beans.

3. *The Amounts of Potash and Phosphoric Acid in the Plants.*

This was, perhaps, the most important part of the investigation. The tables show that the barley plants were able to abstract more than four times as much phosphoric acid and nearly four times as much potash from the original soil as they could from the extracted soil.

From the manner in which the barley grew in the extracted soil, it appeared highly probable that the phosphates and potash were assimilated mainly in the later periods of growth, and that at first the plants were able to obtain very little of these substances from the soil.

With beans, similar results were obtained, except that the plants were able to take much larger quantities from the soil, especially from the extracted soil.

The figures in the table show that the beans grown in the original soil contained more than twice as much potash and more than twice as much phosphoric acid as those grown in the extracted soil.

It would thus appear that beans are more capable than barley of readily assimilating both potash and phosphates. In this connection, it is well to remember that the larger store of plant food contained in the seed of the bean would be able more effectually to tide the young plant over the early period, during which the soil was unable to supply potash and phosphates, than would be the case with the smaller seeds of barley. It is also noteworthy that Dyer, in his determinations of the acidity of the root juices of various plants, found higher values for *Leguminosæ* than for cereals (Trans., 1894, **65**, 133—134). His numbers are as follows:

	Sap acidity.	
	In terms of hydrogen.	In terms of citric acid.
Beans (field grown)............	0·0159	1·11 per cent.
Barley	0·0054	0·38 ,,

After the conclusion of the experiment, the soil from Pots 3, 4, and 7 (extracted soil) were examined by Dyer's method for available potash and phosphoric acid, due allowance being made for the presence of the added sand. As was expected, these soils, which had been deprived of their available plant food at the commencement of the experiment, were found at its conclusion to contain considerable quantities of both potash and phosphates soluble in 1 per cent. solution of citric acid.

The numbers were as follows:

	Available phosphoric acid.	Available potash.
Pot 3	0·021 per cent.	0·0147 per cent.
Pot 4	0·018 ,,	0·0147 ,,
Pot 7	0·010 ,,	0·0072 ,,

These figures show that by the chemical change which went on in the soil during the growth of the plants large quantities of mineral plant food, particularly of potash, became soluble in citric acid solution. In fact, the amount of this regained "available potash" in the case of the barley pots exceeds that removed by treatment with citric acid at the commencement of the experiment (0·0110 per cent.).

These results indicate that soils, under favourable conditions as to moisture, are possessed of remarkable recuperative powers, and that the renewal of the available plant food may take place with considerable rapidity.

Summary.

The general conclusion to be drawn from the results of this investigation is that, whilst Dyer's method affords a satisfactory means of measuring the relative amounts of available plant food in two soils at a given time, it may not accurately gauge their relative fertility, inasmuch as it leaves undetermined the relative rapidity with which the available plant food is renewed by the processes of weathering and decay. However, under similar climatic conditions, the rate will probably be approximately the same for most soils.

The method, therefore, should be of great value in comparing soils, the conditions of which as to climate, &c., are similar. But its indications might lead to erroneous views as to the relative fertility of soils from tropical countries when compared with those in temperate climates, since in the former a smaller amount of available plant food in the soil, if renewed more rapidly, as it probably is, might furnish to the plants an actually greater quantity of nutriment than would be yielded by a soil containing a considerably larger amount of available food, but in which the processes by which the unavailable become available went on more slowly.

Of the probable truth of these conclusions, the writer, from a comparison of his analyses of the soils of the Transvaal with those of English soils, is fully persuaded, although he fully realises the favouring influences of abundant sunshine and high temperature which affect the growth of plants in South Africa, and which help to explain the fact that luxuriant crops are yielded by soils which, on analysis, appear to be extremely deficient in plant food.

The experimental work in connection with this investigation was chiefly carried out in the Agricultural Chemical Laboratories of the Yorkshire College, Leeds, and the author would here gratefully acknowledge the help afforded him by his former colleague, Dr. H. M. Dawson, and by his brother, Dr. Harry Ingle. He is also indebted to Mr. W. H. Dobson for the care exercised in attending to the plants during their growth.

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PRETORIA.

IX.—*The Constitution of Nitrogen Iodide.*

By OSWALD SILBERRAD, Ph.D.

SINCE its discovery in 1812 by Courtois, the explosive compound produced by the action of ammonia on iodine has been repeatedly investigated, with a view to establishing its chemical constitution, but many of the results given in the older chemical literature have been subsequently shown to be erroneous. The difficulties experienced by all workers in investigating the constitution of nitrogen iodide are mainly due to the extreme sensitiveness of the compound in the dry state. Originally, the compound was believed to be simply an iodide of nitrogen containing no other element. Marchand showed, however (*J. pr. Chem.*, 1840, **19**, 1), that when nitrogen iodide was detonated, ammonium iodide was one of the products, thus proving the presence of hydrogen. By combustion over heated lead chromate, he showed that the percentage of hydrogen must be very small.

Bunsen showed (*Annalen*, 1852, **84**, 1) that nitrogen iodide could be prepared from ammonia and iodine in the complete absence of water, thus proving that oxygen was not present. He also showed that the only by-product formed was hydrogen iodide, from which it follows that the reaction is one of direct substitution, and that nitrogen iodide is still a compound of the ammonia type.

The observation of Gladstone (*Chem. Gazette*, 1851, **9**, 269) that ammonia is set free in the preparation of nitrogen iodide from ammonium iodide and bleaching powder does not give any definite indication as to the formula of the compound, although Gladstone considered it an argument in favour of the formula NHI_2.

Szuhay found (*Ber.*, 1893, **26**, 1933) that when ammonia interacted

with iodine, half the iodine was converted into nitrogen iodide, the other half being found as ammonium iodide. This gives no information as to the composition of the nitrogen iodide, however, but only shows that nitrogen iodide is a direct substitution product of ammonia, that is, one molecule of hydrogen iodide (and hence of ammonium iodide) is formed for each atom of iodine which enters into combination with the nitrogen.

Thus, taking, for instance, the formula $N_2H_3I_3$, the formation of nitrogen iodide would be represented by the equation

$$5NH_3 + 3I_2 = N_2H_3I_3 + 3NH_4I.$$

Chattaway's experiments, in which nitrogen iodide was slowly decomposed by a stream of water and the residue analysed, can hardly be regarded as evidence for one formula more than another. In this connection it should be pointed out, firstly, that the ratio of 1 : 2·54 found by him is very little nearer to 1 : 3, which would favour the formation of Stahlschmidt's compound, NI_3 (*Poggendorff's Ann.*, 1862, **115**, 653), than it is to the ratio 1 : 2, which agrees with Szuhay's formula, NHI_2 (*loc. cit.*), and, secondly, that the quantity of free iodine increased so much during the progress of the decomposition (amounting to 44·8 per cent. in the example quoted by Chattaway) that it could probably only be very imperfectly allowed for by the differential method of analysis employed.

The analyses of the products obtained by different workers have led to a number of different formulæ, the following having been put forward by certain of the earlier workers :

NI_3 (Gay-Lussac, Stahlschmidt, Mallet).
NHI_2 (Bineau, Gladstone, Raschig, Szuhay, Seliwanoff).
NH_2I (Millon, Marchand).
$N_2H_3I_3$ and $N_5H_3I_{12}$ (Bunsen).
$N_5H_5I_{10}$ and $N_8H_9I_{15}$ (Guyard).

The conflicting results arrived at by different workers led to the belief that several iodides of nitrogen existed. Indeed, certain investigators found that under different conditions the composition of the products varied. Thus, Stahlschmidt (*loc. cit.*) believed that he produced from aqueous ammonia and an alcoholic solution of iodine a compound having the formula NI_3, whereas from alcoholic ammonia and iodine he obtained a product which he formulated as NHI_2. Mallet (*Chem. News*, 1879, **39**, 257) stated that the concentration of the aqueous ammonia employed influenced the composition of the final product.

Later work has shown that the varying results obtained by different workers were chiefly due to impurities present in the nitrogen iodide

owing to the unsuitable experimental conditions and to the decomposing action of light. Besides this, however, the analytical methods employed were in most instances faulty, and this added to the uncertainty of the results obtained.

The main difficulty in the determination of the composition of nitrogen iodide is due to the fact that the dry substance can only be handled with extreme caution. For this reason, direct analyses with weighed quantities of the dry compound have only recently been carried out. In all the earlier investigations, unknown quantities were treated in various ways, and conclusions were drawn from the ratios between the quantities of the different products. The reagents mainly employed for the decomposition were hydrogen sulphide and sulphurous acid.

Thus Bineau (*Compt. rend.*, 1844, **19**, 764) and, later, Gladstone (*loc. cit.*) used hydrogen sulphide and determined the relative quantities of hydriodic acid and ammonia formed. Bunsen (*Annalen*, 1852, **84**, 1) decomposed the compound with hydrochloric acid and estimated the relative amounts of ammonia and hydriodic acid produced. Mallet (*loc. cit.*) used a solution of sodium sulphite and estimated the nitrogen as ammonia and the iodine as silver iodide. Szuhay (*Ber.*, 1893, **26**, 1933) used free sulphurous acid of known strength and determined the iodine and ammonia. The above methods are, however, all open to objection, since the reduction to ammonia never takes place quantitatively, a certain amount of free nitrogen being always liberated, as was shown by Chattaway (*Amer. Chem. J.*, 1900, **24**, 138). The most satisfactory method is that adopted by this investigator (*loc. cit.*), in which the nitrogen iodide is treated in the dark with standard sodium sulphite; the excess of sulphite is then titrated with standard iodine solution, and the ammonia is subsequently distilled, after the addition of alkali.

In some experiments, Chattaway used weighed quantities of the dry nitrogen iodide, thus gaining an additional check on the results obtained. By means of a series of analyses carried out on products prepared by different methods, Chattaway showed that the same compound was obtained in every instance (*Amer. Chem. J.*, 1900, **23**, 363, 369; 1901, **24**, 138, 159, 318, 331, 342). He found the composition to agree in all cases with the formula originally assigned by Bunsen, namely, $N_2H_3I_3$, and ascertained further that the iodide is a definite chemical compound, neither iodine nor hydriodic acid being present in loose molecular combination, as in periodides or acid iodides. Each atom of iodine was shown to be univalent and directly linked to nitrogen.

Hugot has shown (*Compt. rend.*, 1900, **130**, 505) that at low temperatures compounds exist having the formulæ $N_3H_6I_3$ and $N_4H_9I_3$.

These are, however, only capable of existence in presence of excess of ammonia at very low temperatures, and dissociate very readily, regenerating ammonia and the compound $N_2H_3I_3$. This compound is thus the only one which need be considered at the ordinary temperature.

Although the empirical formula has been thus established, no investigations have hitherto given any insight into the constitution of nitrogen iodide. Evidence as to the structure of the nitrogen iodide molecule can evidently only be obtained by a study of its derivatives. The conclusions drawn from the metallic derivatives have hitherto been rather misleading than otherwise. The compound formulated by Guyard (*Compt. rend.*, 1884, **97**, 526) as $CuI_2,2NH_2I$ cannot be regarded as evidence in favour of the formula NH_2I for nitrogen iodide, for the number of hydrogen atoms in the molecule is difficult to determine by analysis. Thus, whereas the above compound would theoretically contain 0·66 per cent. of hydrogen, a compound having the formula $Cu_2I_2,2NH_3NI_3$ would contain 0·50 per cent., so that no reliable deductions could be made from Guyard's analyses as to the constitution of the compound (compare the following paper).

Szuhay (*Ber.*, 1893, **26**, 1933) obtained a silver derivative of nitrogen iodide, to which he ascribed the formula $AgNI_2$. This appears to render the formula NHI_2 probable for nitrogen iodide. In the following paper, however, the pure compound is shown to be a direct silver derivative of $N_2H_3I_3$.

The reactions of nitrogen iodide with organic compounds have as yet been very little studied. The experiments of Stahlschmidt (*Poggendorff's Ann.*, 1863, **119**, 421) should be noticed, although the conclusions drawn by him from the results were erroneous. By the action of methyl iodide on nitrogen iodide, he obtained the following products: nitrogen, hydriodic acid, ammonium iodide, tetramethylammonium pentaiodide, iodoform, iodine, and, further, a small quantity of an insoluble compound which was not further investigated. From the mother liquor, on addition of caustic potash, he obtained ammonia and di-iodomethylamine.

In view of the conflicting evidence as to the constitution of nitrogen iodide obtained by different authors, the preparation of direct substitution products, which should leave no doubt as to the constitution of this compound, was desirable. The problem has now been definitely solved by a study of the interaction of zinc ethyl and nitrogen iodide. In this way, the formula $NH_3{:}NI_3$ has been established.

Before carrying out this work, the question of the applicability of magnesium alkyl iodides was also considered, as their use would probably be experimentally easier; but since the complete exclusion of alkyl iodides is of great importance, their application was regarded as

unsatisfactory. For the magnesium alkyl iodides may contain traces of alkyl iodide, or may possibly themselves act in an analogous manner to alkyl iodides, which would greatly complicate the reaction. By using zinc ethyl, which could be obtained completely free from iodine compounds, on the other hand, this objection was satisfactorily overcome.

It was established by Chattaway's work that the empirical formula of the compound was $N_2H_3I_3$. From this it is seen that only two different constitutional formulæ are probable, namely, $NH_2I{:}NHI_2$ and $NH_3{:}NI_3$. These two compounds may be assumed to react with zinc ethyl in the manner represented by the equations :

$$\text{I. } 2NH_2I{:}NHI_2 + 6Zn(C_2H_5)_2 = 6Zn(C_2H_5)I + 2C_2H_5{\cdot}NH_2 + 2NH(C_2H_5)_2.$$

$$\text{II. } 2NH_3NI_3 + 6Zn(C_2H_5)_2 = 6Zn(C_2H_5)I + 2NH_3 + 2N(C_2H_5)_3.$$

The latter of these equations was proved to be correct by the identification of ammonia and triethylamine as the products of the reaction.

Experimental.

Preparation of Nitrogen Iodide.—The nitrogen iodide required for this investigation was prepared by allowing iodine chloride to act on aqueous ammonia (compare Bloxam's Chemistry, 4th edition, 1880, p. 180, and also Chattaway and Orton, *J. Amer. Chem. Soc.*, 1900, **23**, 363).

Action of Zinc Ethyl on Nitrogen Iodide.—In the first place, it was necessary to find a solvent for zinc ethyl which would not interact in any way with nitrogen iodide, and preliminary experiments showed that ether was the best suited to the purpose, whilst from the following results it will be seen that the pure solvent is entirely without action on nitrogen iodide. In each experiment, 100 c.c. of ether were used and allowed to remain at 0° for various periods, after which the nitrogen iodide was filtered off and the uncombined iodine in solution shaken out with excess of *N*/10 sodium thiosulphate and estimated. The combined iodine was then estimated by boiling the ether for 24 hours with finely granulated sodium, dissolving the latter in water, and determining the iodine with silver nitrate.

Time during which nitrogen iodide and ether were left together.	Unchanged nitrogen iodide removed (titrated in filtered residue).	Free iodine.	Combined iodine.
(*a*) With methylated ether (sp. gr. 0·720) which had been left for three weeks over ground caustic soda and subsequently distilled.			
1 hour	1·358 grams	0·118	0·0013
4 hours	1·570 ,,	0·135	0·0015
48 ,,	1·326 ,,	0·446	0·0055
(*b*) With the above ether further purified by boiling for twenty-four hours with finely granulated sodium (this ether was used in Experiments 1—4 described below).			
24 hours	5 grams	Not estimated.	Less than 0·0003
(*c*) With ether purified as described below and used in Experiment 5.			
48 hours	5 grams	—	No coloration with starch solution.

On repeating this first series of experiments and allowing the ether to evaporate spontaneously, iodoform was readily detected by its odour; from this it would appear probable that the reaction observed with less carefully purified ether is due to traces of alcohol. Indeed, the reaction appears to lend itself to the detection of very minute traces of alcohol in ether. A suitable diluent having been thus obtained, it became necessary to ascertain the nature of the reaction. To this end, a series of preliminary experiments was carried out with very small quantities of nitrogen iodide, which established the following points:

(*a*) That it is impracticable to work with dry nitrogen iodide in any quantity, as explosions cannot be avoided; it was therefore used under ether.

(*b*) That ammonia is among the products.

(*c*) That the reaction proceeds quietly and slowly, and that even a slight evolution of heat was noticeable only during the addition of the first portion of zinc ethyl.

The following experiments were then carried out, the work being always conducted in red light:

Expt. 1.—Eleven grams of nitrogen iodide (prepared from 100 c.c. of a 14 per cent. solution of iodine chloride) were thoroughly washed by decantation, first with dilute ammonia, then ten times with absolute alcohol, until the latter gave no coloration with anhydrous copper sulphate, and after that as many times with absolute ether which had been prepared by leaving methylated ether (sp. gr. 0·720) over ground caustic soda for three weeks and then boiling for 24 hours with finely granulated sodium. A fresh quantity of absolute ether (50 c.c.) was run in, and then 14 grams of zinc ethyl dissolved in

25 c.c. of ether were introduced. The whole was then left for 48 hours in the dark, after which the mixture was worked up in the manner described below.

On distilling into water the product obtained by the action of the bases on ethyl oxalate, the latter became strongly alkaline. Since ammonia, mono- and di-ethylamines all react with ethyl oxalate, it appeared probable that this base was triethylamine. The quantity, however, was too small to establish its identity.

Expt. 2.—A duplicate experiment was therefore made with 120 grams of nitrogen iodide, and on this occasion the reaction was accompanied by a distinct effervescence, the product showing signs of clogging together, so that it was found necessary to leave the mixture for four days before it could be worked up with safety. On doing so, however, a distinct quantity of the alkaline distillate, which failed to react with ethyl oxalate, was obtained. This was concentrated with excess of hydrochloric acid and treated with a drop of very concentrated platinic chloride solution, when a readily soluble platinichloride was obtained.

0·01677 gave 0·00561 Pt. Pt = 33·45.

$[NH(C_2H_5)_3]_2PtCl_6$ requires Pt = 31·84.

$[NH_2(C_2H_5)_2]_2PtCl_6$ requires Pt = 35·06 per cent.

The quantity was, however, so small that the analytical results were not of sufficient accuracy to be regarded as establishing the nature of the compound.

Expt. 3.—The foregoing experiment was repeated, but in this case the flask was fitted with stirring gear. Unfortunately, the stirrer slipped before many c.c. of the zinc ethyl solution had been added, and, falling on some unchanged nitrogen iodide, caused a violent explosion and considerable conflagration.

Expt. 4.—The experiment was accordingly repeated, and this time successfully; but on working up the product of the action of ethyl oxalate on the bases no better results were obtained.

Expt. 5.—Finally it was decided to work with 1 kilogram of nitrogen iodide, as this, judging from Experiment 2, should yield 0·14 gram of the platinichloride, which ought to be sufficient to obtain a reliable analysis.

It had been noticed throughout that a slight evolution of heat occurred during the addition of the first portions of the zinc ethyl, but as the reaction between zinc ethyl and nitrogen iodide is so slow, the evolution of heat could hardly be traced to this cause; indeed, it appeared far more likely that it was due to the presence of some impurities either in the ether or in the nitrogen iodide. It was therefore decided to exercise the utmost care in order to ensure the

highest degree of purity in both these compounds, and to this end the reaction was carried out in red light and in a refrigerator kept approximately at 0°, the following precautions being observed.

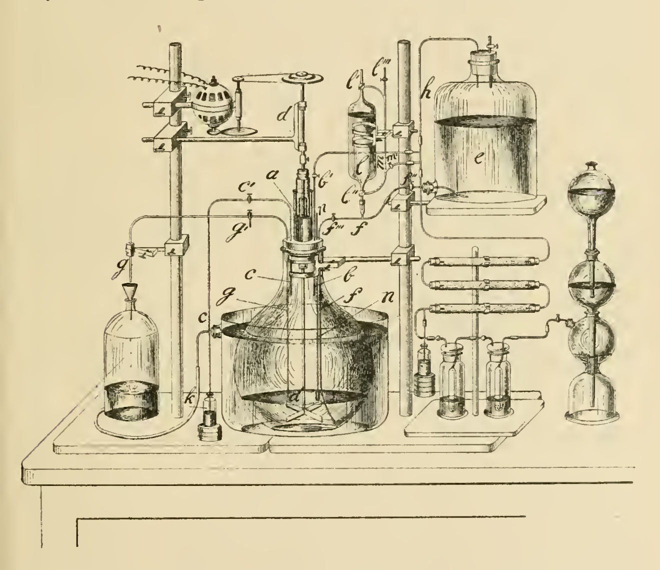
Purification of the Ether.—Two hundred grams of caustic potash, dissolved in 100 c.c. of water, were added to each of 6 "Winchester quarts," each containing 1500 c.c. of methylated ether (sp. gr. 0·720). These bottles were then agitated in a shaking machine for two days, after which the ether was poured on to 1 kilogram of finely ground caustic soda contained in a 10 litre flask immersed in a large water-bath, and the mixture boiled with a reflux condenser for 24 hours. The ether was next decanted into another 10 litre flask, treated with 50 grams of finely granulated sodium, and again boiled for 24 hours, after which it was distilled off. These last two operations were repeated until the ether ceased to tarnish the sodium on boiling for 24 hours. During distillation, the ether was collected in bottles filled with dry carbon dioxide in order to prevent absorption of moisture or auto-oxidation on evaporation.

Purification of the Nitrogen Iodide.—One kilogram of well washed nitrogen iodide was transferred to a 10 litre flask by means of absolute alcohol; it was then further washed 9 times with this solvent, until the liquid gave no coloration with anhydrous copper sulphate, and then ten times with purified ether, 1 litre being used for each washing. The ether used for the last three washings contained no combined iodine, and gave no reaction with nitrogen iodide on standing for 48 hours.

The flask containing 1 kilogram of nitrogen iodide and about 1 litre of ether was then fitted up as shown in the diagram and all the air displaced by means of dry carbon dioxide. The stirrer, *d*, was then set in motion with just sufficient rapidity to cause the nitrogen iodide lying on the bottom of the flask to change its position continuously. A slow stream of pure ether was allowed to flow in from the vessel, *e*, through the tube, *f*, and out through the tube, *g*, the pressures on the surface of the liquid in the flask and in the ether reservoir being rendered identical by means of the carbon dioxide generator, which was connected to the ether reservoir through the tube, *h*, and to the flask through *b*. The tap, *b′*, was so adjusted that a few bubbles of carbon dioxide passed, from time to time, slowly up the tube, *g*, together with the spent ether. The level of the liquid in the flask was thus kept constant. The washing with ether was continued for 4 hours, during which time about 4 litres of pure ether were passed through the flask. The spent ether, after filtration from a few grams of nitrogen iodide which had been carried over, was found to contain very minute traces of free iodine, but no combined iodine whatever.

Action of Zinc Ethyl on the Purified Nitrogen Iodide.—The tube through which the ether made its exit was then closed by means of the cock, *c'*, 2½ litres of pure ether were run into the flask, the displaced carbon dioxide being allowed to escape through the mercury trap, *k*, by means of the tube, *c*, the cock, *c'*, having been previously opened for this purpose.

The flask was then surrounded with a freezing mixture, and as soon as the temperature of its contents had fallen to $-5°$ the addition of zinc ethyl was commenced. In this manner, 1300 grams of zinc ethyl dissolved in 2½ litres of pure ether were added from the container, *l*.* From time to time during the addition of the zinc ethyl, and also at subsequent stages of the experiment, samples were run off by



* The advantages of the piece of apparatus *l* will be obvious from the diagram; it was so constructed that ether could be forced in from the reservoir *e* by means of the carbon dioxide pressure on its surface, and that the whole apparatus could readily be connected with the carbon dioxide system through *m m'*, so that the dry gas displaced the zinc ethyl solution as it flowed through the cock *l''*. The cock *l'''* was attached in order to render it possible to refill the apparatus with zinc ethyl solution, as it was not large enough to hold the complete charge; in doing so, the charge enters through the tap *l'''* and *l''*, whilst the displaced carbon dioxide passes out through *l'*.

means of the three-way cork, c'. In every instance, even after the first addition of a few c.c. of the zinc ethyl, it was found that unaltered zinc ethyl was present in the solution.

The stirring was continued for 48 hours; during the first 24 hours, the refrigerator was kept at 0°, but subsequently was allowed to warm up to the ordinary temperature. The black nitrogen iodide slowly changed into a white, amorphous powder. The reaction proceeded quite quietly, and no evolution of heat was noticeable, indeed, the thermometers in the flask and in the cooling-bath indicated the same temperature during the whole of this period. Half a litre of ether, which had previously been shaken with water, was then added, and as this produced no effervescence it was concluded that the reaction was completed, and excess of water was accordingly added and the mixture again stirred for 24 hours. Excess of hydrochloric acid was then run in and the ether removed by distillation.

At the commencement of the distillation, a large quantity of inflammable gas passed over. A sample of this was collected over mercury, freed from ether vapour, and analysed. It was not absorbed by fuming sulphuric acid or concentrated nitric acid, and proved to be a mixture of paraffins, evidently butane and ethane.

Dry gas before explosion at 99·2° and 757 mm. = 3·2 c.c.
 ,, ,, together with oxygen added at 99·2° and 769 mm. = 53·2 c.c.
Moist gas after explosion at 17·5° and 757 mm. = 36·8 c.c.
 ,, ,, ,, absorbing carbon dioxide with caustic potash at 17·5° and 757 mm. = 29·0 c.c.

The volumetric composition of the gas corresponds with 46 per cent. of butane and 54 per cent. of ethane.

It was foreseen that zinc ethyl would first form double zinc amides with the amines formed (except tertiary amines) with evolution of ethane (Frankland, *Jahresber.*, 1857, 418). These zinc amides hydrolyse readily, however, with hydrochloric acid to zinc chloride and the original amines. Thus the solution contained the hydrochlorides of the amines formed. From these, the bases were liberated with alkali and distilled into hydrochloric acid. The mixture of chlorides obtained on evaporation was then extracted several times with alcohol, in which all the ethylamine hydrochlorides are much more readily soluble than ammonium chloride. The least soluble fraction was recrystallised from water, after which a small portion was converted into its platinichloride and analysed.

0·1182 gave 0·0517 Pt. Pt = 43·74.

$(NH_4)_2PtCl_6$ requires Pt = 43·91 per cent.

The yield of ammonium chloride was 125 grams, or 95 per cent. of the theoretical. For the identification of the organic amines present, Hoffmann and Wallach's method of separation was adopted (*Jahresber.*, 1861, 495; *Annalen*, 1876, **184**, 33). The alcoholic extract of the hydrochlorides was evaporated, distilled with very concentrated caustic soda, and the distillate collected in absolute alcohol at 0°. A slight excess of ethyl oxalate was added and the mixture allowed to remain at a low temperature for 15 hours. On distillation from a water-bath, a strongly alkaline distillate passed over, which proved to be triethylamine.

A crystalline deposit, which formed in the distilling flask, was recrystallised from alcohol, and in this way separated into two compounds. The major portion consisted of ethyl oxamate, melting at 114°.

0·0983 gave 10·4 c.c. moist nitrogen at 16° and 753 mm. N = 12·28.
$CONH_2{\cdot}CO_2{\cdot}C_2H_5$ requires N = 12·0 per cent.

The second product, which was sparingly soluble in alcohol, occurred only in a very small quantity; it melted at 210—211° and probably consisted of oxamic acid. The formation of ethyl oxamate confirmed the presence of ammonia in the original product. The oxamic acid was evidently produced as a by-product of the same reaction. Derivatives of primary or secondary amines were entirely absent.

Since only the tertiary amines are unacted on by ethyl oxalate, it was to be expected that the distillate from the product obtained by the action of the amines on this ester would consist of triethylamine.

The yield was far greater than was expected, and in order to determine it the distillate was made up to 250 c.c. and an aliquot portion titrated with *N*/10 acid with the following result: 3 c.c. required 9·3 c.c. *N*/10 hydrochloric acid; the yield was therefore 7·8 grams or 3·5 per cent.

In order to establish the identity of the base, the remainder of the distillate was acidified with excess of hydrochloric acid, concentrated to a small bulk, and the hydrochloride converted into the readily soluble platinichloride.

0·3704 gave 0·11843 Pt. Pt = 31·98.
$[NH(C_2H_5)_3]_2PtCl_6$ requires Pt = 31·84 per cent.

It thus becomes evident that the reaction is greatly dependent on the experimental conditions. The fact that the success of the reaction demands the entire absence of impurities is a definite proof that the formation of triethylamine is due to the interaction of zinc ethyl on nitrogen iodide, indeed in no other manner can the entire

absence of mono- or di-ethylamine in the presence of so large an excess of ammonia be explained.

My thanks are due to Mr. Smart for his assistance and to the Explosives Committee for permission to publish these results.

RESEARCH LABORATORIES,
ROYAL ARSENAL.

X.—*The Metallic Derivatives of Nitrogen Iodide and their Bearing on its Constitution.*

By OSWALD SILBERRAD, Ph.D.

IN the preceding paper, the author has given a definite proof of the constitution of nitrogen iodide, and has at the same time shown the uncertainty of much of the earlier work. For this reason, it appeared of interest to undertake a revision of the more important work on the derivatives of this compound, because, although a number of derivatives have been obtained by the action of metallic salts on nitrogen iodide or by the action of iodine on ammoniacal salt solutions, great uncertainty exists as to the composition of these substances. A review of this work has shown that both the methods of preparation and of analysis were very unsatisfactory.

The Copper Derivative.—Guyard (*Compt. rend.*, 1884, **97**, 526) ascribed the formula $Cu_2I_2,2NH_2I$ to the compound which he obtained by the action of a potassium iodide solution of iodine on copper ammonium sulphate. He did not, however, support this formula by any analytical data, nor did he give any description of his methods of analysis. Further investigations of the subject have rendered it probable that he deduced the above formula from estimations of the iodine only. He based its relationship to nitrogen iodide on the fact that on treatment with excess of ammonia the copper passed into solution with a simultaneous precipitation of nitrogen iodide.

It must, however, be remarked that the copper compound itself possesses no explosive properties whatever, a circumstance which at once renders Guyard's formula doubtful. The following investigation shows that the compound is a cuprosamine periodide. The compound is prepared by dropping a 20 per cent. solution of potassium iodide (100 c.c.) containing 5 grams of iodine into an aqueous solution containing a slight excess of cuprammonium sulphate in 1200 c.c. of water at the ordinary temperature. The compound separates in small,

crystalline plates. Owing to its insolubility, it cannot be recrystallised from any solvent, and considerable care is therefore necessary for the production of the compound in a pure state. It was found necessary to devise special methods of analysis, and the following procedure was eventually selected as being most satisfactory. The compound was first warmed with dilute alkali and metallic aluminium for half an hour on the water-bath. This brought about complete precipitation of the copper. The precipitate was well washed with hot water, redissolved in a little hot nitric acid, and reprecipitated as cupric oxide and weighed.

After the removal of the copper, the filtrate was acidified in the cold with dilute sulphuric acid and treated with hydrogen peroxide and chloroform to extract the iodine. The chloroform solution was then titrated with standard thiosulphate solution. For the estimation of the nitrogen in this compound, Dumas' method was found to be the most satisfactory.

For comparison, the percentages required by a compound having the formula suggested by Guyard are given in the final column of the following table:

	Found.		$Cu_2I_2,(NH_3)_5I_4,H_2O$ requires	$Cu_2I_2,2NH_2I$ requires
Copper.. ...	12·87	12·96	12·82	19·08
Iodine	76·19	76·43	76·75	76·11
Nitrogen ..	7·53	7·32	7·08	4·21

The compound manifests the characteristics of a periodide in many ways. On heating, it evolves iodine vapour; by treatment with potassium iodide solution, the loosely combined iodine is removed quantitatively, and, on titrating this solution with sodium thiosulphate, the following results were obtained:

Loosely combined iodine found	51·20	51·12 per cent.
$Cu_2I_2(NH_3)_5I_4,H_2O$ requires		51·16 ,,

The behaviour of the cuprosamine periodide towards ammonia, which was taken by Guyard to be indicative of its relationship to nitrogen iodide, must, however, be regarded as distinct evidence of its periodide character. According to the above formulation, the loosely combined iodine interacts with ammonia in a manner precisely similar to that in which potassium periodide acts on ammonia. It thus becomes evident that Guyard's formula for this compound is incorrect, and consequently that its existence is no support of the formula NH_2I for nitrogen iodide.

Cuprosamine Iodide, $Cu_2I_2,NH_3,4H_2O$.—When, in order to remove the loosely combined iodine, the above periodide is treated with potass-

ium iodide—preferably by warming with a 25 per cent. solution—a green, crystalline residue is left, which, when thoroughly washed and dried, is obtained as an olive-green powder insoluble in water, but soluble in ammonia, forming a blue solution.

	Found.		$Cu_2I_2,NH_3,4H_2O$ requires
Copper	27·10	27·21	27·08
Iodine	53·94	54·16	54·03
Nitrogen	3·10	3·02	2·98

By the foregoing treatment, the cuprosamine periodide has therefore lost both iodine and ammonia.

The Silver Derivative.—It was shown by Szuhay (*Ber.*, 1893, **26**, 1933) that a silver compound could be obtained from nitrogen iodide which was in all probability a direct derivative of the latter. He prepared this silver compound by the addition of an ammoniacal solution of silver nitrate to nitrogen iodide suspended in water, and ascribed the formula $AgNI_2$ to the product on the basis of determinations of the ratio of the elements to one another.

It is obvious, however, from Szuhay's paper that insufficient precautions were taken for the production of a pure homogeneous compound; for, since the substance cannot be recrystallised, it is necessary to take extreme care to ensure absolute purity in the first instance. It is hardly to be expected that the conversion of one solid compound into another in this way will give rise to a pure derivative. The heterogeneous character of Szuhay's product is shown by the following analysis of three different preparations carried out exactly as prescribed by him with the exception that the experiments were performed in the dark and at 0° in order to minimise the decomposition of the compounds.

	Analytical results (weight in grams).			Atomic proportions.		
	(1)	(2)	(3)	(1)	(2)	(3)
Nitrogen	0·05623	0·04956	0·05696	4·58	6·98	4·75
Silver	0·09469	0·05479	0·09243	1·00	1·00	1·00
Iodine	0·5364	0·4197	0·5327	4·82	6·51	4·90

These numbers show that it is practically impossible to obtain a homogeneous product by Szuhay's method. The agreement of his analytical results with the formula $AgNI_2$ must therefore have been accidental.

The weak point in Szuhay's procedure appeared to be that the purity of the compound depended on the complete conversion of one insoluble solid into another. This difficulty was overcome in the following manner.

Twenty eight c.c. of a 5 per cent. solution of silver nitrate were added to 30 c.c. of 10 per cent. ammonia; the mixture was then cooled to 0° and treated with 6 c.c. of a 14 per cent. solution of iodine chloride (corresponding with 0·8 gram of iodine) also cooled to 0°. The black precipitate was washed by decantation in the dark.

On attempting to dry this silver derivative, it underwent decomposition with formation of silver iodide. In order to establish its composition, it therefore became necessary to determine the ratio of the elements present by working with the substance suspended in water.

The analytical methods used by Szuhay were examined and found to be open to criticism. He treated the precipitated compound with aluminium turnings in order to reduce the silver to the metallic condition and the nitrogen to ammonia. The ammonia was thereupon distilled off and estimated, the other elements being determined in the residue. He assumed that no loss of nitrogen would take place in this way. Trials of his method have shown, however, that the evolution of traces of nitrogen is practically unavoidable. After trying various methods, the following mode of procedure was found to give the most satisfactory results.

The compound suspended in water is first treated with sodium thiosulphate. The nitrogen is thus converted quantitatively into ammonia, which, after the addition of caustic soda, is distilled off and estimated. The residue is then treated with finely divided aluminium; the silver is thereby reduced to the metallic state and can be filtered off, dissolved in nitric acid, and estimated in the usual way. The iodine remains in solution as sodium iodide and can be readily estimated. The following analytical results were obtained in this way with four different preparations:

	Analytical results (weight in grams).				Atomic proportions.			
	(1)	(2)	(3)	(4)	(1)	(2)	(3)	(4)
Silver	0·1895	0·2141	0·1890	0·2105	1·00	1·00	1·00	1·00
Iodine.. ...	0·6753	0·7252	—	0·7437	3·03	2·88	—	3·01
Nitrogen ..	—	0·0560	0·0525	0·0549	—	2·02	2·14	2·01

The foregoing samples were prepared as follows:

Expts. 1 and 3.—22·8 c.c. of a 5 per cent. solution of silver nitrate were treated with just sufficient 10 per cent. ammonia to redissolve the precipitate, cooled to 0°, and 6 c.c. of a 14 per cent. solution of iodine chloride added.

Expt. 2.—22·8 c.c. of a 5 per cent. solution of silver nitrate were treated with 30 c.c. of 10 per cent. ammonia cooled to 0°, and 6 c.c. of a 14 per cent. solution of iodine chloride added.

Expt. 4.—This specimen was prepared from cyanogen iodide as described below.

The ratio Ag : $\dot{I}$: N is thus undoubtedly 1 : 3 : 2. The compound is therefore derived from nitrogen iodide by the replacement of one atom of hydrogen by silver, and possesses the formula NH_2AgNI_3.

The substance decomposes readily when left at the ordinary temperature, especially when exposed to light. In the dry state, it explodes on the slightest friction.

The Potassium Derivative.—Szuhay observed that the foregoing silver derivative dissolved readily in a solution of potassium cyanide, and that on subsequent addition of ammoniacal silver nitrate the original compound was regenerated. He did not, however, succeed in isolating any soluble derivative.

Regarded in the light of the above investigation, the potassium derivative would receive the formula NI_3NH_2K, and although a silver compound of this formula might well be formed it is very improbable that a direct derivative of potassamide would exist in aqueous solution. In order to gain some insight into the nature of the reaction, the effect of potassium cyanide solution on nitrogen iodide itself was first studied.

Action of Potassium Cyanide on Nitrogen Iodide.—It was observed by Millon, in 1839, that nitrogen iodide dissolves in potassium cyanide, but the products of the reaction have hitherto remained uninvestigated.

For the elucidation of the mechanism of the reaction, experiments were first made to ascertain the relative quantities of nitrogen iodide and potassium cyanide taking part therein. The nitrogen iodide was prepared by the addition of a standard solution of iodine chloride to dilute ammonia. From blank experiments carried out in a precisely similar manner with the same solutions, the yield of nitrogen iodide was found to be 97 per cent. of that calculated from the strength of the iodine chloride solution used. The amount of a standard solution of potassium cyanide necessary to dissolve a known amount of nitrogen iodide prepared as indicated above was then estimated. In this way, 10 c.c. of standard iodine chloride solution, corresponding with 0·385 gram of iodine, were converted into nitrogen iodide and titrated with a standard potassium cyanide (containing 0·01784 gram per c.c.). The volume required to cause complete solution of the nitrogen iodide was (1) 11·27, (2) 11·21, mean = 11·24 c.c.; that is, after correcting for the yield of nitrogen iodide, 1 atom of iodine corresponds with 1·034 molecule of potassium cyanide. Hence one molecule of nitrogen iodide ($NH_3{:}NI_3$) requires 3 molecules of potassium cyanide for its solution. Experiments in which varying quantities of ammonia were used showed that, provided the quantity present is sufficient to suppress the hydrolysis of the cyanide, excess of ammonia is without influence on the amount of potassium cyanide necessary for complete solution of the nitrogen iodide.

For the investigation of the products of the reaction, a quantity of well washed nitrogen iodide was covered with a little ice-cold water, and then treated with a concentrated solution of potassium cyanide, also at 0°, until the black precipitate had disappeared. A white, insoluble residue remained, but this passed into solution on allowing the liquid to attain the ordinary temperature. A quantity of the white residue was collected at 0° and recrystallised from ether; it melted at 146° and its properties agreed with those of cyanogen iodide (m. p. 146·5°). The identity was confirmed by analysis :

0·1715 gave 13·6 c.c. moist nitrogen at 18·5° and 765 mm. N = 9·21.
CNI requires N = 9·18 per cent.

A further quantity of this product was obtained by extracting the solution with ether. A portion of the solution which had not been thus extracted with ether was allowed to evaporate in a vacuum desiccator over concentrated sulphuric acid. Ammonia and cyanogen were evolved, the former in large quantities. As the solution became concentrated, crystals slowly separated; these were collected in four fractions and found to consist of the following salts :

1st Fraction.	KI = 75·0 per cent.	K_2CO_3 = 23·8 per cent.
2nd ,,	KI = 91·9 ,,	K_2CO_3 = 7·99 ,,
3rd ,,	KI = 93·5 ,,	
4th ,,	KI = 78·5 ,,	

The fourth fraction contained, in addition, a quantity of potassium cyanate, which was identified by conversion into urea. With this object in view, the remainder was treated with ammonium sulphate and carefully evaporated to dryness. The residue was dissolved in a little water and a small quantity of 50 per cent. nitric acid added to the cold solution. The crystalline precipitate of urea nitrate which rapidly separated was collected, washed with water and alcohol to remove a small quantity of free iodine present, and further identified by means of the biuret test. The products thus isolated were ammonia, cyanogen, potassium iodide, potassium cyanate, and potassium carbonate.

It was shown above that each molecule of nitrogen iodide required 3 molecules of potassium cyanide for complete solution, thus :

$$3KCN + NH_3NI_3 + 3H_2O = 3CNI + 3KOH + 2NH_3.$$

The cyanogen iodide was partially isolated as such, but if left in solution it gradually interacted with the free potassium hydroxide. The other compounds isolated must be considered as products of this secondary decomposition. Cyanogen chloride is known to yield potassium cyanate when treated with caustic potash. Hence it is not surprising

to find that cyanogen iodide behaves in a similar manner, yielding potassium cyanate and iodide. The potassium carbonate and ammonia found were evidently products of the hydrolysis of potassium cyanate.

As previously shown, the cyanogen iodide is present as an unstable. intermediate product, and is only isolated as a solid compound if the temperature is kept low and the solution sufficiently concentrated to prevent the iodide from dissolving and undergoing further decomposition.

Action of Potassium Cyanide on the Silver Compound.—The foregoing experiments show that the solubility of the silver compound in potassium cyanide is more likely to be due to the formation of cyanogen iodide than to any soluble potassium derivative of nitrogen iodide. In order to elucidate this point, a freshly prepared and carefully washed sample of the silver derivative was suspended in a little water and treated with four molecular proportions of potassium cyanide at 0°. A thick precipitate resulted, which, after filtration, proved to be very sparingly soluble in ether. The soluble portion consisted of cyanogen iodide (m. p. 146°) and the insoluble portion of silver iodide mixed with a small quantity of the cyanide. The aqueous solution yielded, on evaporation, the same compounds as those obtained when nitrogen iodide itself is treated with potassium cyanide, together with a small quantity of silver iodide which separated from solution during evaporation. The reaction is thus to be represented as follows:

$$NI_3NH_2Ag + 4KCN + 4H_2O = 3CNI + AgCN + 4KOH + 2NH_3.$$

As already indicated the production of potassium carbonate was evidently due to secondary reactions.

When the ice-cold solution of the silver derivative in potassium cyanide is allowed to attain the ordinary temperature, cyanogen is evolved, and the precipitate consists only of silver iodide. A second portion of the silver compound was therefore treated with a large excess of potassium cyanide. This increased the formation of cyanogen iodide considerably, upwards of 30 per cent. of the iodine being recovered as such. On acidifying the potassium cyanide solution, after extraction, 61·5 per cent. of the total iodine was recovered as silver iodide. It appears therefore that cyanogen iodide is not stable in presence of silver cyanide unless potassium cyanide is present in sufficient excess to prevent the precipitation of silver iodide.

It still remained, however, to explain the regeneration of the silver compound on the addition of ammoniacal silver nitrate. In order to elucidate this point, the action of cyanogen on ammonia and ammoniacal silver solutions was studied.

Experiment shows that cyanogen iodide does not precipitate nitrogen iodide from ammonia in the absence of silver. If, however, an ammo-

niacal solution of silver oxide, nitrate, or cyanide is added to cyanogen iodide, the silver compound is immediately precipitated.

Thus 22·8 c. c. of a 5 per cent. solution of silver nitrate were treated with 30 c.c. of 10 per cent. ammonia, cooled to 0°, and treated with 50 c.c. of a 2 per cent. solution of cyanogen iodide to which 2 c.c. of 30 per cent. ammonia had been previously added. The washed precipitate gave the following analytical results:

	Ag.	I.	N.
Weight in grams ...	0·2105	0·7437	0·0549
Atomic proportions ...	1·00	3·00	2·09

The mechanism of the regeneration of the silver compound is thus explained. Evidently cyanogen iodide reacts with ammonia, forming traces of nitrogen iodide, but the concentration does not reach the point at which the compound is precipitated. On the addition of silver solution, the more sparingly soluble silver compound at once separates out, and thus, by removing the nitrogen iodide from the sphere of action, admits of its further formation.

In conclusion, I wish to express my thanks to Mr. Smart for his assistance and to the Explosives Committee for permission to publish these results.

RESEARCH LABORATORIES,
ROYAL ARSENAL.

XI.—*The Diazo-derivatives of the Benzenesulphonylphenylenediamines.*

By GILBERT THOMAS MORGAN and FRANCES MARY GORE MICKLETHWAIT.

THE study of the diazo-reaction is often rendered inconclusive owing to the unstable and even explosive character of many of the products, and the authors have been engaged for some time in endeavouring to prepare stable diazonium salts in order to obtain from them well-defined diazo-derivatives which might be useful in investigations bearing on the constitution of compounds of this class.

In the diazonium sulphate of 6-aminocoumarin recently described (Trans., 1904, **85**, 1235), a considerable degree of stability is attained, the dry salt being apparently non-explosive and remaining unchanged for several months.* Nevertheless, the diazocyanides derived from

* Quite recently, a series of stable crystalline chromates has been described by Meldola and Eynon (this vol., p. 1), and Cain (this vol., p. 7) has obtained 4′-hydroxy-3-ethoxydiphenyl-4-diazonium sulphate, a salt which also possesses great stability.

this substance were not so stable as might have been anticipated, and it was therefore not found possible to extend the study of the diazo-reaction in this direction.

Experiments were then instituted with the view of obtaining diazo-derivatives containing an optically active substituent in order that the constitutional changes undergone by these substances under the influence of acids and alkalis might to some extent be traced polarimetrically, even although the products might prove to be too unstable to admit of their being isolated.

d-*Camphor-β-sulphonyl*-p-*nitroaniline,* the substituted sulphonamide produced by the interaction of *p*-nitroaniline and Reychler's *d*-camphorsulphonic chloride, when reduced in such a manner that the camphorsulphonyl group is not eliminated, yields d-*camphor-β-sulphonyl*-p-*phenylenediamine,* $C_{10}H_{15}O{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}NH_2$, an optically active base, the hydrochloric acid solution of which, when diazotised in the ordinary way, yields a diazonium chloride, $C_{10}H_{15}O{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}N_2Cl$. This salt, when treated with dilute aqueous sodium carbonate, sodium acetate, or ammonia, does not yield the corresponding diazo-hydroxide, but gives rise to a sparingly soluble crystalline yellow diazoimide. The analysis of this product indicates that it is formed by the elimination of hydrogen chloride from the diazonium salt, its composition corresponding with the formula:

$$C_6H_4{<}\begin{matrix}N{\cdot}SO_2{\cdot}C_{10}H_{15}O \\ | \\ N_2\end{matrix}.$$

Although compounds of this type have been obtained from certain acyl (acetyl and benzoyl) derivatives of *o*-phenylenediamine (*Annalen*, 1887, **240**, 119; 1888, **249**, 363; *Amer. Chem. J.*, 1895, **17**, 452), this condensation has not hitherto been noticed to occur among the monoacylated *p*-phenylenediamines. The investigation was therefore extended to the simpler case of *benzenesulphonyl*-p-*phenylenediamine*, and the behaviour of this substance towards nitrous acid was compared with that of its ortho- and meta-isomerides under similar conditions.

Benzenesulphonyl-*p*-phenylenediamine, when diazotised in moderately concentrated hydrochloric acid, yields a *diazonium chloride*,

$$C_6H_5{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}N_2Cl,$$

which separates out from the acid solution and is quite stable in the dry state. An aqueous solution of this salt, when treated with sodium acetate, gives rise to a sparingly soluble diazoimide which separates in small, yellow needles, closely resembling the foregoing *d*-camphorsulphonyl derivative. This diazoimide is formed directly when the substituted diamine is treated with sodium nitrite in cold glacial acetic acid.

Benzenesulphonyl-*o*-phenylenediamine, when treated with nitrite in cold hydrochloric acid solution, at once yields a colourless diazo-imide. In this case, the formation of an intermediate diazonium salt could not be detected even when a large excess of acid was employed.

The distinctly yellow hue of the diazoimides derived from *d*-camphor-β-sulphonyl-*p*-phenylenediamine and benzenesulphonyl-*p*-phenylenediamine as contrasted with the colourless appearance of the compound from benzenesulphonyl-*o*-phenylenediamine suggests that the para-derivatives may have a constitution differing from that of the ortho-compound. The diazoimides of the monoacylated *o*-diamines have been hitherto regarded as being derived from aziminobenzene, and in accordance with this view the foregoing colourless ortho-diazoimide (*benzenesulphonyl*-o-*phenylenediazoimide*) should have a constitution represented by the formula

$$C_6H_4\begin{matrix}-N\cdot SO_2\cdot C_6H_5\\ |\\ -N:N\end{matrix}.$$

Since, however, the substance is formed in strongly acid solutions in which the diazo-complex might be expected to exist in the diazonium form, the following alternative configuration,

$$C_6H_4\begin{matrix}-N\cdot SO_2\cdot C_6H_5\\ |\\ -N:N\end{matrix},$$

cannot altogether be ignored. The former formula, containing the five-membered ring, is the more likely, as the formation of the cyclic compound occurs equally readily in the absence of mineral acids. In the case of the isomeric coloured para-diazoimide, two alternative methods of formulating the structure of the compound are possible:

$$C_6H_4\begin{matrix}-N\cdot SO_2\cdot C_6H_5\\ |\\ -N:N\end{matrix} \quad \text{or} \quad \begin{matrix}N\cdot SO_2\cdot C_6H_5\\ \ddot{}\\ C_6H_4\\ N{=}N\end{matrix}$$

I. II.

The former of these formulæ represents the substance as a cyclic para-diazoimide (*benzenesulphonyl*-p-*phenylenediazoimide*), whereas the latter indicates a quinonoid configuration (*benzenesulphonylimino*-p-*benzoquinonediazide*). With this substance there can scarcely be any question of a diazonium structure, since the compound is not formed until the diazonium chloride is decomposed by sodium acetate or a weak alkali.

The difference in stability between the colourless ortho-diazoimide and the yellow para-diazoimide is very great. The former is not more sensitive to light than other colourless, aromatic acylated bases, and may be boiled with 50 per cent. aqueous caustic potash without undergoing any change; moreover, it is not attacked by concentrated hydrochloric acid. The latter is extremely sensitive to light, its bright yellow colour changing to a dull brown on exposure for a few hours; it is decomposed into resinous products by hot aqueous alkalis, or even by boiling water, and it readily dissolves in cold concentrated hydrochloric acid to regenerate quantitatively the original benzenesulphonyl-*p*-aminobenzenediazonium chloride which subsequently crystallises from the acid solution.

Further experiments will be made in order to ascertain within what limits the formation of these coloured para-diazoimides is possible, and whether the condensation occurs when other acyl groups are substituted for the benzenesulphonyl complex. In this connection, it is of interest to notice that Nietzki, who first diazotised acetyl-*p*-phenylenediamine, does not record the formation of an acetyl-*p*-diazoimide of this type (*Ber.*, 1884, **17**, 344).

Benzenesulphonyl-m-*phenylenediamine* differs considerably from its two isomerides in its interaction with nitrous acid and does not appear to have any tendency to form a cyclic diazoimide by internal condensation. When diazotised in moderately concentrated hydrochloric acid, it yields a *diazonium chloride* which separates out from the acid solution. This salt is, however, less stable than the corresponding para-compound, and, when washed with water or alcohol until free from acid, it undergoes partial decomposition and acquires a red tint. This change may be brought about more readily by the action of aqueous sodium acetate, when a molecule of the diazonium salt loses its diazo-nitrogen and becomes converted into a phenolic derivative which at once condenses with a second molecule of the diazonium salt to form a somewhat ill-defined, yellowish-red azo-compound, which has a composition corresponding approximately with the formula

$$C_6H_5 \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OH) \cdot NH \cdot SO_2 \cdot C_6H_5.$$

This change is complete in about 30—40 minutes, even at the ordinary temperature, the amount of nitrogen eliminated agreeing closely with the quantity required by theory.

The distinctive character of the behaviour of each of the three benzenesulphonylphenylenediamines towards nitrous acid disappears when the iminic hydrogen atom of the substituent, $C_6H_5 \cdot SO_2 \cdot NH$, is replaced by a methyl group. as-*Benzenesulphonylmethyl*-m-*phenylenediamine* yields a *diazonium chloride*, the aqueous solution of which is not appreciably affected by sodium acetate. as-*Benzenesulphonylmethyl-*

o-*phenylenediamine* also gives rise to a *diazonium chloride*, the formation of a cyclic diazoimide by internal condensation being no longer possible; this is also true of the diazonium salt derived from as-*benzenesulphonylmethyl*-p-*phenylenediamine.* That these diazo-compounds are really normal diazonium salts is shown by condensing them with β-naphthol in alkaline solution, when, in each case, an insoluble azo-β-naphthol derivative is at once precipitated.

The diazonium salts from *d*-camphorsulphonyl-*p*-phenylenediamine and the benzenesulphonyl derivatives of *m*- and *p*-phenylenediamines also yield azo-compounds with β-naphthol, but in these instances the products at first remain dissolved in the alkaline solution and afterwards separate slowly in the form of sparingly soluble alkali derivatives, which are readily decomposed by acetic acid, yielding the free azo-β-naphthols. This difference in the behaviour of the two series of azo-β-naphthol derivatives is undoubtedly due to the acidic character of the iminic hydrogen of the complex $RSO_2 \cdot NH-$ which is present in the latter series, the azo-derivative losing its acidic character in aqueous solution when this hydrogen atom is replaced by methyl as in the azo-compounds derived from the three *as*-benzenesulphonylmethylphenylenediamines.

The foregoing results indicate that in order to study the diazo-reaction more completely with the optically active base containing the camphor residue it will be necessary to alkylate the group

$$-NH \cdot SO_2 \cdot C_{10}H_{15}O,$$

and thus prevent the formation of the cyclic diazoimide by internal condensation. Experiments with this end in view are in progress, together with others having for their object the more extended examination of the new series of acyl para-diazoimides, the existence of which has been demonstrated by the investigations described in this paper.

Experimental.

d-*Camphor-β-sulphonyl*-p-*nitroaniline*, $C_{10}H_{15}O \cdot SO_2 \cdot NH \cdot C_6H_5 \cdot NO_2$, was prepared by heating together on the sand-bath 10 parts of Reychler's *d*-camphorsulphonic chloride with 12 parts of *p*-nitroaniline (2 mols.) in 30 parts of toluene. At first the substances mixed completely, yielding a clear solution, but a precipitate rapidly formed which, after two hours, was removed and the filtrate further heated, when a second crop of the solid was obtained. The product was dissolved by boiling with excess of aqueous sodium carbonate, the solution was allowed to cool until the excess of *p*-nitroaniline had again separated, when tho *d*-camphorsulphonyl derivative was precipitated from the

filtrate with hydrochloric acid and crystallised from dilute alcohol, being finally obtained in lustrous, amber-coloured needles melting at 145°.

0·1972 gave 0·3963 CO_2, 0·1046 H_2O. C = 54·82 ; H = 5·89.
0·1920 „ 12·6 c.c. nitrogen at 17·5° and 775 mm. N = 7·78.
0·1799 „ 0·1242 $BaSO_4$. S = 9·48.
$C_{16}H_{20}O_5N_2S$ requires C = 54·80 ; H = 5·67 ; N = 7·95 ; S = 9·10 per cent.

d-*Camphor-β-sulphonyl*-p-*phenylenediamine*,
$C_{10}H_{15}O·SO_2·NH·C_6H_4·NH_2$.

The foregoing nitro-compound (6 grams), suspended in 200 c.c. of hot water acidified with 1 gram of glacial acetic acid, was treated with 6 grams of iron filings; the mixture was boiled for about an hour after the introduction of the metal, rendered alkaline with 1·8 grams of potassium hydrogen carbonate, and filtered rapidly at the pump. Since the benzenesulphonyldiamine has sufficiently acidic properties to remain dissolved in the alkaline solution, the filtrate was neutralised with acetic acid and then allowed to crystallise. The greater part of the base remained in the oxide of iron precipitate, and was extracted therefrom by boiling alcohol. The total yield from the alcoholic and aqueous solutions was 5 grams.

The new diamine is insoluble in light petroleum (b. p. 60—80°), but dissolves in water, chloroform, acetone, ethyl acetate, benzene, or toluene; it crystallises most readily from its solutions in alcohol or pyridine, and separates in almost colourless, acicular prisms melting at 186°. Prolonged boiling with these solvents tends to darken the product.

0·2099 gave 16·25 c.c. nitrogen at 15·5° and 760 mm. N = 9·08.
0·2537 „ 0·1893 $BaSO_4$. S = 10·24.
$C_{16}H_{22}O_3N_2S$ requires N = 8·70 ; S = 10·00 per cent.

A specimen of the base crystallised from pyridine and dissolved in acetone was examined in the polarimeter: 0·4084 in 25 c.c. of acetone gave $\alpha = 1·50°$, whence $[\alpha]_D = +45·8°$.

d-Camphor-β-sulphonyl-*p*-phenylenediamine (4 grams) was diazotised in 8 c.c. of hydrochloric acid (sp. gr. 1·17) diluted with 100 c.c. of ice-water by the action of 6 c.c. of 20 per cent. sodium nitrite solution. The clear solution thus obtained was divided into two equal parts, one of which was filtered and treated with excess of aqueous sodium acetate. The yellow, crystalline precipitate which rapidly separated was collected and washed successively with water, alcohol, and light petroleum. d-*Camphor-β-sulphonyl*-p-*phenylenediazoimide*, $C_6H_4{:}[N_3]·SO_2·C_{10}H_{15}O$, thus obtained, was analysed without further purification.

0·1672 gave 18·7 c.c. nitrogen at 18° and 756 mm. N = 12·85.
$C_{16}H_{19}O_3N_3S$ requires N = 12·61 per cent.

This substance decomposes violently at 118—120° when quickly heated, but when the temperature is raised more slowly it darkens at this temperature and gradually chars, becoming quite black above 200°.

The new diazoimide, although decomposed on boiling with alcohol, may be crystallised from benzene, but in this case also prolonged digestion with the hot solvent causes decomposition. It dissolves in cold concentrated hydrochloric acid or in 50 per cent. sulphuric acid to form the corresponding colourless diazonium salt, which couples with alkaline β-naphthol, yielding the following azo-derivative.

d-*Camphor-β-sulphonyl*-p-*aminobenzene-azo-β-naphthol*,
$C_{10}H_{15}O·SO_2·NH·C_6H_4·N:N·C_{10}H_6·OH$,
was prepared by adding the second portion of the diazotised solution to a solution of β-naphthol in cold aqueous caustic soda, when a gelatinous, dark red substance was slowly precipitated; this compound redissolved on warming the solution, and a dark, granular precipitate with a green reflex separated on cooling. This product, which appeared to be a sodium derivative, was dissolved in hot glacial acetic acid and the free azo-β-naphthol separated on cooling in dark red, nodular crystals with a green, metallic lustre; it melted at 192°.

0·4183 gave 31·5 c.c. nitrogen at 19° and 733 mm. N = 8·81.
$C_{26}H_{27}O_4N_3S$ requires N = 8·80 per cent.

The Benzenesulphonylnitroanilines.

These compounds, which have already been described by Lellmann (*Ber.*, 1883, **16**, 596; *Annalen*, 1883, **221**, 16), were prepared by heating 1 mol. of benzenesulphonic chloride with 2 mols. of the nitroaniline dissolved in toluene. This condensation is effected most easily in the case of the meta-base, and least readily with the ortho-isomeride. In each case, the crude product after evaporating off the toluene was boiled with an excess of aqueous sodium carbonate until the whole mass had dissolved. The solution, when allowed to cool, deposited the excess of nitroaniline (1 mol.), and the filtrate on acidification with hydrochloric acid yielded the benzenesulphonyl derivative, which was purified by repeated crystallisation from dilute alcohol; the yields given below were in each case obtained from 28 grams of the nitroaniline and 18 grams of the acid chloride.

Benzenesulphonyl-*p*-nitroaniline separated in pale yellow, prismatic needles melting at 139° (Lellmann gave 139°); the yield was about 29 grams.

Benzenesulphonyl-*m*-nitroaniline crystallised in prismatic crystals melting at 133·5° (Lellmann gave 131—132°); the yield was 31 grams.

Benzenesulphonyl-*o*-nitroaniline crystallised in tabular prisms and melted at 104° (Lellmann gave 104°); the yield was 13 grams.

The Benzenesulphonylphenylenediamines.

The nitro-compounds described in the preceding section were reduced with iron filings and hot water acidified with a small amount of acetic acid.

Benzenesulphonyl-p-*phenylenediamine*, $C_6H_5 \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot NH_2$, was readily obtained in almost quantitative yield by suspending the corresponding nitro-compound (7 grams) in 50 c.c. of hot water acidified with 1 gram of glacial acetic acid and gradually adding 5 grams of iron filings. As there was no spontaneous action, the mixture was boiled for 30—40 minutes, 50 c.c. of hot water being added as the reduction proceeded. After introducing 1·5 grams of sodium hydrogen carbonate, the mixture was rapidly filtered whilst hot; the filtrate, when cooled and neutralised with acetic acid, deposited a small crop of acicular crystals, but as the greater portion of the substituted diamine remained in the oxide of iron precipitate this residue was extracted with boiling alcohol. The extract, when filtered and cooled, deposited colourless crystals, which were recrystallised from the same solvent and then melted at 173°.

0·3150 gave 32 c.c. nitrogen at 19° and 747 mm. N = 11·48.
0·2724 ,, 0·2543 $BaSO_4$. S = 12·81.
$C_{12}H_{12}O_2N_2S$ requires N = 11·29; S = 12·90 per cent.

The method of reduction and extraction adopted in the foregoing preparation was also applied in producing benzenesulphonyl-*o*-phenylenediamine, which has already been described by Lellmann (*loc. cit.*), who gave its melting point as 168°. Our preparation, which crystallised from dilute alcohol in acicular prisms, melted at 165—167°.

0·1836 gave 18·3 c.c. nitrogen at 19° and 752 mm. N = 11·33.
$C_{12}H_{12}O_2N_2S$ requires N = 11·29 per cent.

The yield obtained by this method of reduction was almost quantitative.

Benzenesulphonyl-m-*phenylenediamine* was produced by reducing 7 grams of the corresponding nitro compound with 5 grams of iron filings, 100 c.c. of hot water (added in 2 instalments), and 1 gram of glacial acetic acid. In this experiment, the boiling was discontinued 15 minutes after the last lot of metal had been introduced; 1·5 grams

of sodium hydrogen carbonate were then added and the mixture rapidly filtered. The residue was extracted with alcohol, which, however, in the case of this isomeride deposited very little of the base on cooling. The crude product was purified by crystallisation from water containing a little alcohol, some animal charcoal being employed to decolorise it. The purified base crystallises in pearly plates melting at 98—99°; it is somewhat too soluble to crystallise well from ethyl acetate, acetone, or the alcohols.

0·1222 gave 12·2 c.c. nitrogen at 19° and 756 mm. N = 11·42.
$C_{12}H_{12}O_2N_2S$ requires N = 11·29 per cent.

Benzenesulphonyl-*m*-phenylenediamine, when suspended in water and treated successively with diazobenzenesulphonic acid and sodium carbonate, at once yields a deep red, soluble azo-colouring matter. Under these conditions, its ortho- and para-isomerides at first give a negative result, but in both cases the mixture subsequently develops a yellowish-brown coloration.

Action of Nitrous Acid on Benzenesulphonyl-o-*phenylenediamine.*

Benzenesulphonyl-o-*phenylenediazoimide*, $C_6H_4{:}[N_3]{\cdot}SO_2{\cdot}C_6H_5$, is obtained by adding an aqueous solution of sodium nitrite (1 mol.) to a suspension of benzenesulphonyl-*o*-phenylenediamine hydrochloride in cold hydrochloric acid. It may also be prepared by adding the nitrite to a solution of the diamine in glacial acetic acid, when it separates in small, colourless needles melting at 130°. The yield of the diazoimide by the former method of preparation is practically quantitative. The compound may be crystallised from benzene, but prolonged boiling with this solvent produces a discoloration of the product.

0·1274 gave 18·4 c.c. nitrogen at 18° and 744 mm. N = 16·32.
0·2562 „ 0·2263 $BaSO_4$. S = 12·14.
$C_{12}H_9O_2N_3S$ requires N = 16·21; S = 12·35 per cent.

Three determinations of the molecular weight by the cryoscopic method in benzene gave M. W. = 229, 252, 243, the theory requiring M. W. = 259.

Action of Nitrous Acid on Benzenesulphonyl-p-*phenylenediamine.*

Benzenesulphonyl-p-*aminobenzenediazonium chloride*,

$$C_6H_5{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}N_2Cl,$$

separates out as a bulky precipitate of colourless, felted needles on adding aqueous sodium nitrite to a solution of the *p*-diamine in excess of hydrochloric acid (3 parts of concentrated acid: 10 parts of water); when collected and washed successively with water, alcohol, and light

petroleum, it was dried in the desiccator, and then gave the following result on analysis:

0·1680 gave 19·8 c.c. nitrogen at 16·5° and 764·5 mm. N = 13·77.
$C_{12}H_{10}O_2N_3ClS$ requires N = 14·21 per cent.

This salt dissolves in cold water, giving a faintly acid reaction with litmus paper. On mixing this solution with one of β-naphthol in aqueous caustic potash, an azo-compound was immediately produced, but at first this substance remained dissolved, and afterwards gradually separated in the form of its potassium derivative.

*Benzenesulphonyl-*p*-aminobenzeneazo-β-naphthol,*
$C_6H_5{\cdot}SO_2{\cdot}NH{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_{10}H_6{\cdot}OH$,
is produced by dissolving the preceding potassium compound in glacial acetic acid; the solution on cooling deposits scarlet needles melting at 239°.

0·2788 gave 25·0 c.c. nitrogen at 19° and 760 mm. N = 10·31.
$C_{22}H_{17}O_3N_3S$ requires N = 10·42 per cent.

The foregoing diazonium salt yields azo-colouring matters with "R salt" and also with "chromotrope acid," but in the former case the development of colour takes place much more slowly than with β-naphthol.

*Benzenesulphonyl-*p*-phenylenediazoimide,* $C_6H_4{:}[N_3]{\cdot}SO_2{\cdot}C_6H_5$, crystallises out in yellow needles when the aqueous solution of the foregoing diazonium chloride is either treated with excess of sodium acetate or rendered alkaline with ammonia or sodium carbonate. It may also be prepared directly by adding aqueous sodium nitrite to a cold solution of benzenesulphonyl-*p*-phenylenediamine in glacial acetic acid.

This diazoimide is very insoluble in the organic media, but when obtained, by either of the foregoing methods, washed successively with water, alcohol, and light petroleum, and dried in the desiccator, it is sufficiently pure for analysis.

0·2900 gave 40·3 c.c. nitrogen at 18° and 757 mm. N = 16·00.
0·1104 ,, 0·1000 $BaSO_4$. S = 12·44.
$C_{12}H_9O_2N_3S$ requires N = 16·21; S = 12·36 per cent.

The substance decomposes violently at about 155°; it rapidly darkens on exposure to light, but may be preserved without change in the dark. It is insoluble in cold aqueous caustic alkali and is resinified by the boiling solution; alcoholic potash decomposes it giving rise to a phenolic substance, which gives a reddish-brown coloration with diazobenzenesulphonic acid. The diazoimide, when added to cold concentrated hydrochloric acid, rapidly dissolved, and, on adding a few

fragments of ice to the solution, benzenesulphonyl-*p*-aminobenzenediazonium chloride separated in colourless, felted needles; this salt was characterised by the formation of the azo-β-naphthol derivative.

Action of Nitrous Acid on Benzenesulphonyl-m-*phenylenediamine.*

Benzenesulphonyl-m-*aminobenzenediazonium chloride*,

$$C_6H_5 \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot N_2Cl,$$

was produced by slowly adding aqueous sodium nitrite (1 mol.) to a cold suspension of the substituted *m*-diamine in excess of strong hydrochloric acid, and carefully triturating the mixture in a mortar until the whole was of a creamy consistence. The precipitate was then collected at the pump and washed successively with water, alcohol, and light petroleum. During this operation, the white, sparingly soluble diazonium salt assumed a reddish tint. The chlorine was estimated in a portion of the dried product, but the result indicated that some of the diazonium chloride had undergone hydrolysis. The substance was accordingly characterised by means of its azo-β-naphthol derivative.

Benzenesulphonyl-m-*aminobenzeneazo-β-naphthol*,

$$C_6H_5 \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot N\colon N \cdot C_{10}H_6 \cdot OH,$$

produced in the ordinary way from the foregoing diazonium chloride and β-naphthol, slowly separates from the alkaline solution in the form of an ill-defined potassium derivative; this is decomposed by glacial acetic acid yielding the azo-β-naphthol, which separates from its solutions in this solvent as bright red, hard, prismatic and nodular crystals, melting at 218° and having a metallic lustre.

0·1316 gave 12·10 c.c. nitrogen at 18° and 773 mm. N = 10·80.
$C_{22}H_{17}O_3N_3S$ requires N = 10·42 per cent.

The diazonium chloride of benzenesulphonyl-*m*-phenylenediamine, when dissolved in cold dilute hydrochloric acid and treated with excess of sodium acetate, yields an orange-red precipitate, the production of which is accompanied by an elimination of nitrogen. The precipitate was washed with water and dried on porous plate. This compound was with difficulty obtained in a crystalline form by repeated extraction with benzene. The final product melted indefinitely at 156—169°.

0·1014 gave 10·0 c.c. nitrogen at 17° and 770 mm. N = 11·60.
0·1020 ,, 0·0897 $BaSO_4$. S = 12·10.
$C_{24}H_{20}O_5N_4S_2$ requires N = 11·02; S = 12·59 per cent.

These results agree approximately with the formula of an azo-compound produced in the following manner:

$$2C_6H_5 \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot N_2 \cdot OH = N_2 + H_2O + C_6H_5 \cdot SO_2 \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(OH) \cdot NH \cdot SO_2 \cdot C_6H_5.$$

The nitrogen evolved in the condensation was estimated by carrying out the process on known quantities of the diazonium chloride placed in a volumeter. Weighed amounts of the *m*-diamine were diazotised in the manner previously indicated and the diazotised product rinsed with hydrochloric acid into the outer vessel of the volumeter, whilst a strong solution of sodium acetate was placed in the inner tube. The two liquids were thoroughly mixed at the ordinary temperature and the evolved nitrogen measured: N = 5·92 (over water), 5·63, 5·64 (over mercury); the theory requires N = 5·64 per cent.

The azo-compound develops a brownish-red coloration with concentrated sulphuric acid.

When diazotised in glacial acetic acid, benzenesulphonyl-*m*-phenylenediamine yields a dark brownish-red, gelatinous product which gave an intense blue coloration with concentrated sulphuric acid.

The diazonium chloride of the *m*-diamine, when added to a solution of the base itself in glacial acetic acid, gave a yellowish-red azo-compound which developed a deep red coloration with concentrated sulphuric acid.

Preparation of the as-*Benzenesulphonylmethylphenylenediamines.*

Benzenesulphonylmethyl-p-*nitroaniline*, $C_6H_5 \cdot SO_2 \cdot N(CH_3) \cdot C_6H_4 \cdot NO_2$, was readily prepared by heating 5 grams of benzenesulphonyl-*p*-nitroaniline (1 mol.) and 1·1 grams of caustic potash (1 mol.) in 25 c.c. of alcohol, to which are gradually added 3·5 grams of methyl iodide mixed with 25 c.c. of alcohol, the boiling being continued during 4 to 6 hours. At first a crystalline precipitate of the potassium derivative, $C_6H_5 \cdot SO_2 \cdot NK \cdot C_6H_4 \cdot NO_2$, was produced, but this gradually dissolved to an almost colourless solution. The solvent was partially evaporated and a little water was added, when the methyl derivative separated in hard, massive crystals which were insoluble in aqueous potassium hydroxide, 4—5 grams being thus obtained. The new compound readily crystallised from alcohol in transparent, pale yellow crystals, which, after recrystallisation, melted at 120°.

0·4818 gave 40·3 c.c. nitrogen at 18° and 765 mm. N = 9·73.
$C_{13}H_{12}O_4N_2S$ requires N = 9·58 per cent.

Benzenesulphonylmethyl-o-*nitroaniline* was produced by methylating benzenesulphonyl-*o*-nitroaniline in the manner indicated in the preceding experiment, but only half the quantity of alcohol was employed. The product separated in large plates and on recrystallisation from alcohol was obtained in the form of colourless needles melting at 118—119°.

0·2027 gave 17·0 c.c. nitrogen at 18° and 774 mm. N = 9·85.
$C_{13}H_{12}O_4N_2S$ requires N = 9·58 per cent.

Benzenesulphonylmethyl-m-*nitroaniline*.—This compound was prepared just like its ortho-isomeride. In this case, however, there was far less separation of potassium derivative. On evaporating off the alcohol, an oil separated which hardened on stirring. This product was very soluble in benzene, ethyl acetate, and the alcohols, but insoluble in petroleum; it was crystallised from a mixture of benzene and light petroleum (b. p. 40—60°), when it separated in rosettes of colourless needles melting at 83°.

0·2769 gave 23·6 c.c. nitrogen at 18° and 772 mm. N = 10·00.
$C_{13}H_{12}O_4N_2S$ requires N = 9·58 per cent.

Reduction of the Benzenesulphonylmethylnitroanilines.

In the preliminary experiments on the reduction of the preceding methylated nitro-derivatives, it was found that this reaction took place much less readily than in the case of the unmethylated compounds. Accordingly, larger amounts of acetic acid and water were employed with a greater excess of iron, and the heating was continued for a longer time, usually about 2 hours; the following were found to be convenient proportions: 1 part of the methylated nitro-compound, 1 part of glacial acetic acid, 2 parts of iron filings, and 30—40 parts of hot water. After neutralising with sodium hydrogen carbonate, the aqueous solution was filtered and the residue extracted with alcohol. A small portion of the base separated from the aqueous solutions, but the larger quantity was obtained from the alcoholic extracts.

as-*Benzenesulphonylmethyl*-p-*phenylenediamine*,
$$C_6H_5\cdot SO_2\cdot N(CH_3)\cdot C_6H_4\cdot NH_2,$$
crystallises from dilute alcohol in colourless, prismatic needles or elongated plates melting at 119°.

0·1490 gave 13·4 c.c. nitrogen at 19° and 755 mm. N = 10·29.
$C_{13}H_{14}O_2N_2S$ requires N = 10·68 per cent.

as-*Benzenesulphonylmethyl*-o-*phenylenediamine* crystallises from dilute alcohol in colourless needles melting at 116°.

0·2650 gave 24·4 c.c. nitrogen at 17° and 771 mm. N = 10·83.
$C_{13}H_{14}O_2N_2S$ requires N = 10·68 per cent.

as-*Benzenesulphonylmethyl*-m-*phenylenediamine*, obtained like its isomerides, crystallises from water and alcohol in lustrous, colourless

needles, or from a mixture of benzene and light petroleum in fern-like aggregates of prismatic crystals; it melts at 96°.

0·1196 gave 10·9 c.c. nitrogen at 18° and 766 mm. N = 10·61.
$C_{13}H_{14}O_2N_2S$ requires N = 10·68 per cent.

Diazotisation of the as-*Benzenesulphonylmethylphenylenediamines.*

The foregoing diamines readily dissolve in hydrochloric acid, and their solutions, when treated with sodium nitrite, furnish soluble diazonium chlorides which do not undergo condensation on treatment with sodium acetate; the solutions remain quite clear, and when they are added to a solution of β-naphthol in aqueous alkali, insoluble azo-compounds are produced in every case.

A similar result is obtained when the nitrite is added to solutions of the bases in glacial acetic acid, and there is no tendency on the part of *as*-benzenesulphonylmethyl-*m*-phenylenediamine to form a complex azo-compound such as is produced when the unmethylated base is diazotised in this manner (compare p. 84).

The diazonium chlorides of the *as*-benzenesulphonylmethylphenylenediamines yield sparingly soluble crystalline platinichlorides.

Benzenesulphonylmethyl-p-*aminobenzeneazo-β-naphthol*,

$$C_6H_5 \cdot SO_2 \cdot N(CH_3) \cdot C_6H_4 \cdot N \colon N \cdot C_{10}H_6 \cdot OH,$$

separates as a brick-red precipitate and crystallises from alcohol in lustrous, cardinal-red plates and flattened needles; it melts at 162·5° and develops a crimson coloration with concentrated sulphuric acid.

0·1736 gave 15·6 c.c. nitrogen at 18° and 775 mm. N = 10·59.
$C_{23}H_{19}O_3N_3S$ requires N = 10·31 per cent.

This azo-compound is insoluble in aqueous alkalis or benzene, moderately soluble in alcohol, and dissolves very freely in glacial acetic acid.

Benzenesulphonylmethyl-o-*aminobenzeneazo-β-naphthol.*—When the aqueous solution of benzenesulphonylmethyl-*o*-aminobenzenediazonium chloride is rendered ammoniacal, a pale yellow, amorphous precipitate is obtained which probably consists of a diazo-hydroxide. This mixture, when added without filtration to the alkaline β-naphthol solution, at once gives an orange-coloured azo-derivative which readily crystallises from alcohol or ethyl acetate in bright red leaflets melting at 191°.

0·1836 gave 16·6 c.c. nitrogen at 18·5° and 770 mm. N = 10·61.
$C_{23}H_{19}O_3N_3S$ requires N = 10·31 per cent.

With concentrated sulphuric acid, this azo-compound develops a cherry-red coloration.

Benzenesulphonylmethyl-m-aminobenzeneazo-β-naphthol. — When *as*-benzenesulphonylmethyl-*m*-phenylenediamine is diazotised in hydrochloric or acetic acid and the diluted solution added to an alkaline β-naphthol solution, a brownish-orange azo-compound separates. This substance crystallises from alcohol in red prisms melting at 129—131°.

0·1848 gave 16·6 c.c. nitrogen at 17° and 771 mm. N = 10·59.
$C_{23}H_{19}O_3N_3S$ requires N = 10·31 per cent.

This azo-derivative develops a reddish-violet coloration with concentrated sulphuric acid.

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XII.—*The Reduction Products of Anisic Acid.*

By JOHN SCOTT LUMSDEN.

WHEN anisic acid, dissolved in amyl alcohol, is treated with sodium, the products of reduction are hexahydrobenzoic acid and δ-ketohexahydrobenzoic acid.

This reduction was first carried out by me in Baeyer's laboratory in 1895 (*Inaug. Diss. München*), but I was unable to identify the crystalline acid, easily soluble in water, which was produced along with the hexahydrobenzoic acid. It was expected to be δ-hydroxyhexahydrobenzoic acid, but analysis did not confirm this, and the usual tests failed to show the presence of a hydroxyl group.

Recently (Trans., 1904, **85**, 416), Perkin has prepared synthetically δ-ketohexahydrobenzoic and δ-hydroxyhexahydrobenzoic acids, and I find that the product of reduction of anisic acid agrees in every property with the δ-keto-acid.

The formation of hexahydrobenzoic acid from anisic acid may be represented thus:

$$C_6H_4(O\cdot CH_3)(CO_2H) + 8H = CH_2\begin{matrix} \diagup CH_2\cdot CH_2 \diagdown \\ \diagdown CH_2\cdot CH_2 \diagup \end{matrix} CH\cdot CO_2H + CH_3\cdot OH;$$

the methoxy-group is split off and the ring completely hydrogenated. This removal of the alkoxy-group seems to be a general action, as it

has been found to take place when *o*-ethoxybenzoic and 2-hydroxy-3-methoxybenzoic acids are reduced (Einhorn and Lumsden, *Annalen*, 1895, **286**, 257).

It is more difficult to understand the formation of δ-ketohexahydrobenzoic acid from anisic acid. This may take place by the addition of four hydrogen atoms, then the methyl group in presence of strong alkali would be replaced by hydrogen, and this hydrogen, as usually happens in the case of the hydrogen of a hydroxyl group adjacent to a double bond, would be transferred to the next carbon atom, thus:

```
                 O·CH3          O·H            O
                 |              |              ||
 O·CH3           C              C              C
  /\            / \\           / \\           / \
 |  |   -->   CH2  CH   -->  CH2  CH   -->  CH2  CH2 .
 |  |          |    |         |    |         |    |
  \/          CH2  CH2       CH2  CH2       CH2  CH2
 CO2H           \ /            \ /            \ /
                 CH             CH             CH
                 |              |              |
                 CO2H           CO2H           CO2H
```

To confirm this view of the action, several attempts were made to obtain the keto-acid from *p*-hydroxybenzoic acid by means of sodium and amyl alcohol, but without success; the acid remained unaltered. It is, however, possible that the change takes place by the addition of four hydrogen atoms, then by the agency of one molecule of water the methyl is removed as methyl alcohol, and hydrogen is added to the γ-carbon atom, thus:

```
 O·CH3  OH            O      + CH3·OH
 |      |             ||
 C      |             C
 / \\   |            / \
CH2  CH  H     =   CH2  CH2                .
|    |              |    |
CH2  CH2           CH2  CH2
  \ /                \ /
  CH                 CH
  |                  |
  CO2H               CO2H
```

This interpretation is not improbable when it is remembered how frequently changes taking place in concentrated alkaline solutions may be represented by the interaction of the elements of water.

The Reduction of Anisic Acid.

Ten grams of acid and 150 c.c. of amyl alcohol were placed in a round-bottomed litre flask which was connected to a condenser by a branched tube, the upright limb of which held a dropping funnel. The flask was supported on an asbestos basket and heat applied until all the acid was dissolved and the alcohol boiled; the funnel was then removed

and 5 grams of sodium were dropped in. There was an immediate separation of the sodium salt of the acid, and soon sodium amyloxide appeared as a gelatinous mass and the contents of the flask became a pasty solid. Ten grams of sodium were then added, and while the heating was continued the flask was shaken to prevent the solid adhering to the glass. Gradually the contents of the flask liquefied, and in about 30 minutes a clear fluid was obtained. More sodium and alcohol were added from time to time, until in all 30 grams of sodium had been used together with 300 c.c. of alcohol. The contents of the flask were now allowed to cool to about 100°, then an equal volume of water was added; this decomposed the sodium amyloxide and the alcohol formed a layer on the surface. When the liquid was quite cold, the alcohol was separated, washed twice with water, and the washings added to the alkaline fluid. This fluid was boiled for some time to drive off dissolved alcohol, cooled, and acidified. It was then extracted three times with ether, and the residue, after distilling off the solvent, was a mixture of unaltered anisic acid, hexahydrobenzoic acid, and δ-ketohexahydrobenzoic acid.

The keto-acid is very soluble in water, whilst the other two acids are very sparingly soluble. The residue was therefore shaken with several small quantities of water, and when these were evaporated to a small volume, crystals of the keto-acid separated out, and, after drying on a porous tile, were recrystallised.

The hexahydrobenzoic acid was obtained free from anisic acid by steam distillation. The voluminous distillate was neutralised with sodium carbonate, evaporated to a small volume, acidified, and extracted with ether. From the ether, the hexahydrobenzoic acid was obtained as a pale yellow oil. The yield varies, but from 10 grams of anisic acid 7 grams of hexahydrobenzoic acid and 1 gram of the δ-keto-acid have been obtained. When greater quantities of anisic acid are used at one operation, there is a smaller percentage of reduced products.

δ-Ketohexahydrobenzoic Acid, $CO(CH_2\cdot CH_2)_2\colon CH\cdot CO_2H$.—This substance is very soluble in water, and separates from solution in crystals containing 1 mol. of water of crystallisation. Good crystals are obtained from a mixture of ligroin and ether (m. p. 67°).

0·3330 acid heated for two hours at 110° lost 0·0356 H_2O or 11·56 per cent., the calculated loss for 1 mol. water being 11·26 per cent.

0·1875 of the dried acid gave 0·4068 CO_2 and 0·1213 H_2O. C = 59·17; H = 7·18.

$C_7H_{10}O_3$ requires C = 59·16; H = 7·04 per cent.

Calcium Salt, $[CO(CH_2\cdot CH_2)_2\colon CH\cdot CO_2]_2Ca,H_2O$.—This was prepared by warming a solution of the acid with calcium carbonate,

filtering, and evaporating; it forms long, silky needles with 1 mol. of water.

0·2154 heated at 110° lost 0·0126 water or 5·84, the calculated loss for 1 mol. water being 5·29 per cent.

0·2027 dried salt gave 0·0849 $CaSO_4$ or 12·32, the calculated amount being 12·43 per cent.

The *barium salt* was prepared like the calcium salt, but using barium carbonate; it is very soluble in water, and definite crystals could not be obtained as there is decomposition during evaporation.

0·2330 gave 0·1321 $BaSO_4$ or Ba = 33·30, the calculated value being Ba = 32·70 per cent.

The Semicarbazone.—This compound separates at once when semicarbazide hydrochloride is added to a solution of the acid mixed with sodium acetate. It is a fine, white powder, sparingly soluble in water and insoluble in ether or benzene; it softens at 198°, and at 199° melts and decomposes.

The properties of the keto-acid and the semicarbazone correspond exactly with those observed by Perkin.

To obtain pure hexahydrobenzoic acid from the product of reduction, the acid obtained from several operations was dried in ether and distilled under reduced pressure. After the first few drops had passed, a perfectly colourless distillate was obtained, boiling at 115—117° under 13 mm. pressure. The acid distilled under the ordinary pressure without apparent decomposition, the boiling point being 232—233°. On standing, or at once on cooling in ice, crystals of the acid separate, but the whole liquid does not solidify. The crystals are large and well formed, and when freed from adhering liquid acid by drying on a porous plate they melt at 29°. The properties of this acid and its derivatives are detailed in the succeeding paper.

XIII.—*The Physical Properties of Heptoic, Hexahydrobenzoic, and Benzoic Acids and their Derivatives.*

By John Scott Lumsden.

By the reduction of anisic acid, as described in the preceding paper, a quantity of hexahydrobenzoic acid was obtained in a very pure state. This is the simplest acid with a hexamethylene ring, and for the purpose of gaining information regarding the physical properties of

this ring formation the derivatives of hexahydrobenzoic acid have been prepared and compared with the corresponding derivatives of heptoic acid, in which the six carbon atoms form a chain, and with benzoic acid, in which the six carbon atoms form a benzene nucleus. It was particularly desirable to obtain a knowledge of the influence of the presence of a hexamethylene ring on the boiling point, the molecular volume, and the molecular refraction of a compound, and these constants have been carefully determined. The acids and their derivatives will be first described, and then by arrangement in tabular form their relationships will be made evident.

Hexahydrobenzoic Acid, $CH_2(CH_2{\cdot}CH_2)_2{:}CH{\cdot}CO_2H$.—This substance as prepared from anisic acid is a colourless liquid, which boils at 232·5° under the ordinary pressure. It crystallises, on cooling, in well-formed, monoclinic prisms, which melt at 29° and, on exposure to the air, become wet and lose their glassy appearance. Although the acid is soluble in most organic solvents, it separates from these always as a liquid, and crystals could only be obtained by cooling the distilled acid. The presence of traces of water or other impurity prevents the acid crystallising. In the solid state, hexahydrobenzoic acid is almost odourless, but when liquid or in solution in volatile solvents it has a most disagreeable rancid odour, not unlike valeric acid. The solubility of the acid in water is very small, as 100 grams of water at 15° only dissolve 0·201 gram, or the solubility is 0·201 100/15°. The sp. gr. of the liquid acid at 15° was obtained by using an apparatus with capillary ends, which allowed of the determination being made before crystallisation took place. The value found was 1·0480 15°/4°, and the molecular volume was therefore $128/d = 122{\cdot}4$ c.c. The refractive index for sodium light, using a Pulfrich's refractometer, was R Na/15° 1·46952.

The electrical conductivity at 25° was as follows :

M.W. in litres.	μ.	μ_∞ 374·5 100 m.	$K = 100k$.
64	10·40	2·777	0·00123
128	14·72	3·941	0·00125
256	20·97	5·601	0·00128
512	29·19	6·021	0·00128
1024	40·63	10·800	0·00128

Affinity constant K = 0·00126

A quantity of liquid hexahydrobenzoic acid was obtained from Kahlbaum, which, on cooling and adding a crystal of the pure acid, partially solidified. This acid was of good quality, and was used to prepare a few of the following derivatives.

Esters of Hexahydrobenzoic Acid.—These esters, which were prepared by the action of hydrogen chloride on a solution of the acid in

excess of the alcohol, are fragrant liquids; their physical constants are as follows:

	B. p.	Sp. gr. 15°/4°.	Mol. wt./d.	R Na/15°.
Methyl ester	183·0°	0·9954	143·1	1·45372
Ethyl ,, ...	196·5	0·9672	161·3	1·45012
Propyl ,, ...	215·5	0·9530	178·3	1·44862

Hexahydrobenzoyl Chloride, $CH_2(CH_2{\cdot}CH_2)_2{:}CH{\cdot}COCl$.—This was obtained by treating the acid with rather more than the calculated quantity of phosphorus pentachloride in a distilling flask. After the action was completed, the phosphorus oxychloride was distilled off at 107°, and the new product was obtained between 180° and 190°. After fractionation, the acid chloride was obtained pure as a colourless liquid boiling at 184° and with a pungent odour resembling benzoyl chloride.

Sp. gr. 1·0962 15°/4°, mol. wt./d = 133·6, R Na/15° = 1·47662.

Hexahydrobenzoic Anhydride, $\begin{matrix} CH_2(CH_2{\cdot}CH_2)_2{:}CH{\cdot}CO \\ CH_2(CH_2{\cdot}CH_2)_2{:}CH{\cdot}CO \end{matrix}\!\!>\!O$.

To obtain this substance, the sodium salt of hexahydrobenzoic acid was prepared and carefully dried at 140°; it was then powdered and added in slight excess to freshly distilled hexahydrobenzoyl chloride. Warming took place, the odour of the chloride disappeared, and the new odour of the anhydride became apparent. After heating at 100° to complete the action and then cooling, the anhydride was extracted by dry benzene from the sodium chloride and unaltered sodium salt of the acid. When the benzene was distilled off, the anhydride was fractionated and obtained as a colourless liquid with a faint characteristic odour. On cooling in ice, a mass of soft crystals was obtained, and, after being dried on a porous tile, the crystals melted at 25°. The constants for the liquid anhydride are: b. p. 280—283°, sp. gr. 1·0585 15°/4°, mol. wt./d = 224·85, R Na/15° = 1·48189.

Hexahydrobenzamide, $CH_2(CH_2{\cdot}CH_2)_2{:}CH{\cdot}CO{\cdot}NH_2$.—This amide was prepared by the action of phosphorus pentachloride on the acid, the product being poured into concentrated ammonium hydroxide saturated with ammonium carbonate. The amide separated at once, and, after crystallising several times from water and dilute alcohol, it was obtained in fatty flakes melting at 184°. Markownikoff prepared this compound and found that it melted at 185—186°.

Hexahydrobenzanilide, $CH_2(CH_2{\cdot}CH_2)_2{:}CH{\cdot}CO{\cdot}NH{\cdot}C_6H_5$.—To obtain this substance, the acid was heated for several hours with a small excess of aniline. A solid mass separated on cooling, and this, after washing with dilute hydrochloric acid, was dried and crystallised from alcohol. The anilide forms flat, silky plates melting at 139°.

Heptoic Acid, $CH_3(CH_2)_5 \cdot CO_2H$, *and its Derivatives.*

The following compounds have been prepared from heptoic acid obtained from Kahlbaum by the same methods used for the preparation of the derivatives of hexahydrobenzoic acid. The boiling points given are, however, those very carefully determined by Perkin (Trans., 1884, **45**, 484) and Gartenmeister (*Annalen*, 1886, **233**, 249).

	M. p.	B. p.	Sp. gr. 15°/4°.	Mol. wt./*d*.	*R* Na/15°.
Heptoic acid.........	−10°	223·0° (P.)	0·9212	141·1	1·42505
Methyl ester.........	—	172·1 (G.)	0·8806	163 5	1·41366
Ethyl ,, ...	—	187·1 (G.)	0·8714	181·3	1·41436
Propyl ,, ...	—	206·4 (G.)	0·8682	198·1	1·41835
Heptoyl chloride...	—	175·0 (P.)	0·9669	153·5	1·43447
Heptoic anhydride.	17	255—258	0·9217	262·5	1·43346
Heptamide	96	—	—	—	—
Heptanilide	71	—	—	—	—

The solubility of heptoic acid in water was found to be 0·241 100/15°, and the affinity constant, calculated from the conductivity at 25° by Franke (*Zeit. physikal. Chem.*, 1895, **16**, 463), is $K = 0·00131$.

Benzoic Acid and its Derivatives.

These compounds were either obtained from Kahlbaum or specially prepared. The values given for the boiling points are those found by Perkin (Trans., 1896, **69**, 1025) or they are the mean values of the observations of other workers.

Benzoic acid melts at 121·5° and boils at 249·2°. The solubility in water was found to be 0·258 100/50°, and the affinity constant at 25° calculated by Kohlrausch from the determination of the conductivity by Ostwald is $K = 0·0060$.

The sp. gr. of the solid acid was obtained by melting a weighed quantity in a sp. gr. bottle, the rest of the bottle being filled with aniline. By this means, air bubbles were effectually removed. The value found was 1·2659 at 15°/4°. As the sp. gr. of heptoic and hexahydrobenzoic acids were determined in the liquid state, in order that benzoic acid might be compared with them, it was necessary to find, if possible, what the sp. gr. of benzoic acid would be if it were liquid at 15°. At the melting point, the sp. gr. of benzoic acid is 1·0800 (Schiff, *Annalen*, 1884, **223**, 264), and, assuming that the rate of expansion is the same as that of heptoic acid (Zander, *Annalen*, 1884, **224**, 92), the sp. gr. would be 1·1470 at 15°/4°. The sp. gr. was then determined in benzene solution, it being assumed that the benzene undergoes no change in volume. A solution containing 4·0076 grams of acid and 95·9924 grams of benzene had a sp. gr. of 0·89071, whilst the sp. gr. of the

benzene was 0·88249. From these numbers, the sp. gr. of the dissolved acid was 1·1463 at 15°/4°, which is like the value deduced from the comparison with heptoic acid. The sp. gr. in benzene solution is therefore taken as the sp. gr. of the acid if it were liquid at the same temperature. The molecular volumes are: $122/d$ liquid = 106·42; solid = 96·37.

The index of refraction was determined in the same benzene solution. Kanonnikoff (*Ber.*, 1883, **16**, 3048) has shown that the refraction of a solution is the sum of the refractions of the dissolved body and the solvent, therefore $P\frac{N-1}{D} = p\frac{n-1}{d} + p'\frac{n'-1}{d'}$, where P, p, and p' are the weights of solution, solid, and solvent respectively, these values being multiplied by the corresponding specific refractions. If the weight P is made 100, and p and p' are given in percentages, the equation arranged for finding the specific refraction of the dissolved body is $\frac{n-1}{d} = 100\frac{N-1}{D} - (100-p)\frac{n'-1}{d'}\Big/p$. 4·0076 grams of benzoic acid in 95·9924 grams of benzene had a refractive index of 1·50531, that of the benzene being 1·50420, therefore $\frac{n-1}{d} = 0·47084$. If the sp. gr. is 1·1463, the refractive index is (0 47084 × 1·1463) + 1 = 1·53974 Na/15°.

The properties of the derivatives of benzoic acid are as follows:

	M. p.	B. p.	Sp. gr. 15°/4°.	Mol. wt./*d*.	*R* Na/15°.
Methyl ester.........	—	198·6° (P.)	1·0937	124·4	1·52049
Ethyl ,, ...	—	211·8 (P.)	1·0509	142·8	1·50790
Propyl ,, ...	—	230 7 (P.)	1·0274	159·6	1 50139
Benzoyl chloride ...	—	199·0	1·2188	115·3	1·55799
Benzoic anhydride .	42°	360·0	1·1989	188·5	1·57665
Benzamide	130	—	—	—	—
Benzanilide	160	—	—	—	—

In the following table, the constants of the three acids and their derivatives are arranged for the purpose of comparison:

		Heptoic.	Hexahydrobenzoic.	Benzoic.
Acids:	Melting points	−10°	29°	121·5°
	Boiling points	223°	232·5°	249·2°
	Sp. gr. 15°/4°	0·9212	1·0480	1·1463
	Molecular volume 15°...	141·1	122·4	106·42
	Refractive index Na/15°	1·42505	1·46952	1·53974
	Solubility 15°	0·241	0·201	0·258
	Affinity constant *K*......	0·00131	0·00126	0·0060
Methyl esters:	Boiling points	172·1°	183°	198·6°
	Sp. gr.	0·8806	0·9954	1·0937
	Molecular volume	163·5	143·1	124·4
	Refractive index	1·41366	1·45372	1·52049

		Heptoic.	Hexahydrobenzoic.	Benzoic.
Ethyl esters:	Boiling points	187·1°	196·5°	211·8°
	Sp. gr.	0·8714	0·9672	1·0509
	Molecular volume	181·3	161·3	142·8
	Refractive index	1·41436	1·45012	1·50790
Propyl esters:	Boiling points	206·4°	215·5°	230·7°
	Sp. gr.	0·8682	0·9530	1·0274
	Molecular volume	198·1	178·3	159·6
	Refractive index	1·41835	1·44862	1·50139
Acid chlorides:	Boiling points	175°	184°	199°
	Sp. gr.	0·9669	1·0962	1·2188
	Molecular volume	153·5	133·6	115·3
	Refractive index	1·43447	1·47662	1·55799
Acid anhydrides:	Melting points	17°	25°	42°
	Boiling points	256°	282°	360°
	Sp. gr.	0·9217	1·0585	1·1989
	Molecular volume	262·5	224·85	188·5
	Refractive index	1·43346	1·48189	1·57665
Acid amides:	Melting points	96°	184°	130°
Acid anilides:	Melting points	71°	139°	160°

It is seen that the values of the properties of hexahydrobenzoic acid and its compounds are intermediate between those of heptoic and benzoic acids. The melting points, boiling points, specific gravities, and refractive indices are higher than those of heptoic, and lower than those of benzoic acid, with the exception of the melting point of the amide, which is higher than that of either of the two corresponding compounds. The solubility of the acids is in each case very small, and that of hexahydrobenzoic acid is slightly lower than the others. The affinity constant of the hexahydro-acid is considerably lower than that of benzoic acid, and is very similar to that of an acid of the fatty series. The relationship of the boiling points is worthy of further consideration. As the corresponding derivatives of the acids differ by the same number of hydrogen atoms and the same changes in constitution, it was to be expected that there would be a considerable regularity in the differences of the boiling points. That this is the case is seen from the following table :

Boiling Points.

	Acid.		Acid chloride.		Methyl ester.		Ethyl ester.		Propyl ester.
Heptoic	223·0	48·0	175	1·5	173·5	13·6	187·1	19·3	206·4
	9·5		9		9·5		9·4		9·1
Hexahydrobenzoic...	232·5	48·5	184	1·0	183·0	13·5	196·5	19·0	215·5
	16·7		15		15·6		15·3		15·2
Benzoic	249·2	50·2	199	0·4	198·6	13·2	211·8	18·9	230·7

There is an increase of about 9° from the heptoic to the hexahydrobenzoic series, and of about 15° from that to the benzoic series. The boiling point of benzoic acid itself, given by Kopp (*Jahresber.*, 1855, **8**, 35), seems to be about 2° too high. The difference between the boiling point of the acid and any particular derivative is seen to be the same in each series, bringing out the interesting fact that if two acids have about the same molecular weight, whether they belong to the fatty, the hexamethylene, or benzoic series, the substitution of the hydroxyl of the acids by an element or group will produce the same change of boiling point in each case. The difference for CH_2 is, as usual, smaller between the methyl and ethyl esters than between the ethyl and propyl esters due to the association of the methyl compounds, and the table shows a further example of the fact, first pointed out by Schroder (*Ber.*, 1883, **16**, 1312), that the boiling points of the acid chloride and methyl ester of the same acid lie very close together.

The Molecular Contraction due to the Presence of a Hexamethylene Ring.

From the observations of Traube, the volume of the molecular weight in grams of a substance in the liquid state can be calculated by adding to the sum of the atomic volumes the co-volume of 25·9 c.c. This rule holds strictly for organic compounds in which the carbon atoms form a chain, but when a benzene ring is present in the molecule a contraction of 13·2 c.c., due to the shrinking in volume in the formation of the ring, must be allowed for. The following table shows that there is exactly the same diminution in volume due to the presence of a hexamethylene ring:

Molecular Volumes 15°.

		Acid.		Acid chloride.		Methyl ester.		Ethyl ester.		Propyl ester.	Anhydride.
Heptoic	Found	141·1	12·4	153·5	10·0	163·5	17·8	181·3	16·8	198·1	262·5
	D	3·2		0·7		2·2		0·5		−0·2	−0·9
	Calc...	144·4	9·8	154·2	11·5	165·7	16·1	181·8	16·1	197·9	261·6
	d	18·7		19·9		20·4		20·0		19·8 (19·4)	37·7
Hexahydrobenzoic.	Found	122·4	11·2	133·6	9·5	143·1	18·2	161·3	17·0	178·3	224·8
	D	2·7		1·2		3 2		1·1		0·2	−2 0
	Calc...	125·1	9·7	134·8	11·5	146·3	16·1	162·4	16·1	178·5	222·8
	d	16·0		18·3		18·7		18·5		18·7 (18·6)	36·3
Benzoic	Found	106·4	8·9	115·3	9·1	124·4	18·4	142·8	16·8	159·6	188·5
	D	0·1		0·9		3·3		1·0		0·3	−2·9
	Calc...	106·5	9·7	116·2	11·5	127·7	16·1	143·8	16·1	159·9	185·6

The values found represent the volumes in c.c. of the molecular weight in grams at 15°. The values calculated are the sum of the

atomic volumes as given by Traube, namely, carbon 9·9, hydrogen 3·1, carbonyl, ester, and anhydride oxygen 5·5, hydroxyl oxygen 0·4, co-volume 25·9, with a deduction for each benzene and hexamethylene ring of 13·2 c.c. The differences between the actual and the calculated volumes are given in the lines *D*, and in lines *d* are set down the differences between the actual volumes in the adjacent series, the calculated values being noted at the ends of the lines. The members in each series are seen to vary in a similar manner; the acids and methyl esters are lower by 2—3 c.c. than the calculated values, owing to association, except in the case of benzoic acid, the volume of which was determined in benzene solution, where association was obviated, but the other numbers are as close as the errors of experiment would lead one to expect.

The point of importance is, that when 13·2 c.c. are deducted from the sum of the atomic volumes the values are as close to the actual volumes in the case of the hexahydrobenzoic as in that of the benzoic compounds, showing that the volumes of a hexamethylene and a benzene ring are identical.

It is usually assumed, by consideration of the tension theory of Baeyer as to the constitution of the benzene nucleus, that an expansion of the ring occurs when it becomes hydrogenated, but, whatever the structural change may be when that takes place, it is here proved that it must be of such a nature that it is accompanied by no alteration in volume of the nucleus.

A hexamethylene ring has no influence on the refraction of a compound: In the table on p. 98, the refraction constants for the three acids and their derivatives are given. The first column contains the refractive index, the second the specific refraction, the third the molecular refraction, the fourth the molecular refraction calculated from the sum of the atomic refractions, the values used being those deduced for sodium light by Zecchini (Abstr., 1893, ii, 253), namely, carbon 4·71, hydrogen 1·47, hydroxyl oxygen 2·65, carbonyl oxygen 3·33, chlorine 10·05; the last column contains the differences between the actual and the calculated values.

The sum of the atomic refractions is seen to agree closely with the real molecular refractions in both the heptoic and hexahydrobenzoic series, therefore the hexamethylene structure exerts no influence on the refraction of light. In the benzoic series, the sum of the atomic refractions is much less than the molecular refractions, and about nine units must be added to represent the additional refraction due to the benzene nucleus. It will be noticed that the molecular refractions of the corresponding benzoic and hexahydrobenzoic compounds are almost identical, although the latter contain six hydrogen atoms more, showing that the benzene nucleus causes a retardation of light as

	R Na/15° = n.	$\frac{n-1}{d}$.	$\frac{n-1}{d}M$.	Sum atomic refractions.	Diff.
Heptoic acid	1·42505	0·5526	59·98	59·53	0·45
Hexahydrobenzoic acid ...	1·46952	0·4478	57·34	56·59	0·75
Benzoic acid	1·53974	0·4708	57·44	47·77	9·67
				(56·59)	0·85
Methyl heptoate	1·41366	0·4697	67·64	67·18	0·46
,, hexahydrobenzoate	1·45372	0·4558	64·91	64·24	0·67
,, benzoate	1·52049	0·4759	64·72	55·42	9·30
				(64·24)	0·48
Ethyl heptoate	1·41436	0·4756	75·15	74·83	0·32
,, hexahydrobenzoate .	1·45012	0·4654	72·59	71·89	0·70
,, benzoate	1·50790	0·4833	72·50	63·07	9·43
				(71·89)	0·61
Propyl heptoate	1·41835	0·4818	82·87	82·48	0·39
,, hexahydrobenzoate.	1·44862	0·4708	80·02	79·54	0·48
,, benzoate	1·50139	0·4880	80·03	70·72	9·31
				(79·54)	0 49
Heptoyl chloride	1 43447	0·4493	66·74	65·46	1·28
Hexahydrobenzoyl chloride	1·47662	0·4348	63·70	62·52	1·18
Benzoyl chloride	1·55799	0·4578	64·32	53·70	10·62
				(62·52)	1·80
Heptoic anhydride	1·43346	0·4702	113·79	113·47	0·32
Hexahydrobenzoic ,,	1·48189	0·4553	108·36	107·59	0·77
Benzoic anhydride	1·57665	0·4810	108·70	89·95	18·75
				(107·59)	1·11

great as that due to six hydrogen atoms. When this value, namely, $6 \times 1·47 = 8·82$, is added to the sum of the atomic refractions of the benzoic compounds, the numbers given in brackets are obtained and the differences between these and the real values are seen to be similar in the other series, therefore 8·82 represents the refraction of the benzene ring.

The results of the foregoing investigation may be summarised as follows: the properties of hexahydrobenzoic acid and its derivatives are intermediate between those of heptoic and benzoic acids. In the case of the boiling points, the hexahydro-derivatives boil 9° higher than those of heptoic and 15° lower than those of benzoic acid. The volume of a hexamethylene ring is identical with that of a benzene nucleus, but whilst a hexamethylene ring exerts no influence on the refraction of light, the retardation by a benzene nucleus is equal to that due to six hydrogen atoms, so that corresponding derivatives of benzoic and hexahydrobenzoic acids have the same molecular refraction.

I beg to acknowledge my indebtedness to the Chemical Society for a grant from the Research Fund to provide the materials required in this investigation.

XIV.—*Transformations of Derivatives of* s-*Tribromodiazobenzene.*

By KENNEDY JOSEPH PREVITÉ ORTON.

IN studying the reactions of the *s*-trihalogendiazobenzenes, the author observed (*Proc. Roy. Soc.*, 1902, **71**, 153; Trans., 1903, **83**, 796) that under certain well-defined conditions a halogen atom occupying the ortho-position was displaced by a hydroxyl group, a quinonediazide (diazophenol) being produced, thus:

N_2 / Br Br / Br $\longrightarrow$ N_2 / Br :O / Br + HBr.

According to the author's observations, the conditions favouring this interchange were the simultaneous presence in solution of the hydroxyl ion, $(OH)'$, and the diazonium ion, $(C_6H_2Br_3{\cdot}N_2)^{\cdot}$. Thus the salts of a strong acid, the sulphate, &c., do not suffer this decomposition. Similarly, the diazotates in the presence of excess of hydroxide, that is, when the ions $(OH)'$ and $(C_6H_2Br_3{\cdot}N_2O)'$, but not the ion $(C_6H_2Br_3{\cdot}N_2)^{\cdot}$, are in solution, are also stable.

In the course of this investigation, the author had occasion to repeat the experiments in which Hantzsch and Pohl (*Ber.*, 1902, **35**, 2964) obtained *s*-tribromophenylnitrosoamine, $C_6H_2Br_3{\cdot}NH{\cdot}NO$. According to these chemists, this substance is formed under the very conditions in which the author observed the production of the quinonediazide. Hantzsch and Pohl found that the nitrosoamine was produced on cautiously neutralising solutions of the diazotates, or in the decomposition of dilute solutions of diazonium salts of weak acids. They failed to observe the elimination of bromine, and believed that the amorphous, yellow substance which is formed under these conditions consisted only of the nitrosoamine. According to the author, this yellow material consisted in all cases observed by him of a mixture of a complex substance or substances, probably azo- or hydroxyazo-derivatives, and 3 : 5-dibromoquinonediazide, which formed under the most favourable conditions some 25 per cent. of the mixture.* On no occasion was any evidence of the presence of Hantzsch and Pohl's nitrosoamine obtained.

In a subsequent paper, Hantzsch (*Ber.*, 1903, **36**, 2069), as a

* For further comparisons between the materials described by Hantzsch and Pohl and Orton respectively, see Orton, Trans. 1903, **83**, 798.

consequence of the author's results, modified some of the statements previously made, now finding that bromine is eliminated always in the decomposition of *s*-tribromodiazobenzene under the conditions described above, the quinonediazide being produced. Further, he admits that the substance previously described as the hydrochloride of the nitrosoamine is in fact the hydrochloride of the quinonediazide. He, however, still claims that the nitrosoamine is formed and is present in the yellow solid, although he no longer describes it as a stable substance, but states that it decomposes at any but a low temperature, hydrogen bromide and the quinonediazide being formed. He ascribes the author's failure to recognise the presence of the nitrosoamine to the fact that the author worked at too high a temperature; below 0°, the nitrosoamine does not decompose so rapidly. He concludes that the author is in error in representing the decomposition as being primarily a replacement of bromine by hydroxyl. Under all conditions, he believes that the nitrosoamine is the first product of the change of a diazonium salt or diazotate, and that it subsequently decomposes into the quinonediazide with the elimination of bromine.

On account of the discrepancy between these series of observations, and still more from the fact that from the author's point of view it is important that it should be decided whether the quinonediazide is formed directly from the diazo-compounds, a view which all the author's experience with these substances has gone to confirm (Trans., 1903, **83**, 799, &c.), or through the intermediary stage of the nitrosoamine, a fresh series of experiments has been made to investigate the decomposition of *s*-tribromodiazobenzene.

Since in any case it is now admitted that the *s*-tribromophenylnitrosoamine is unstable and cannot be isolated free from quinonediazide, &c., in an analysable condition, it now only remains to be demonstrated that the product first formed at low temperatures contains the nitrosoamine, and secondly that this product can be shown to decompose into quinonediazide or other substances with the elimination of bromine. If it can be shown that the yellow product of the decomposition not only contains quinonediazide, but also that the proportion of diazide neither increases, nor do any subsequent decompositions take place, then it would appear that generally, at least, no nitrosoamine is formed under these conditions, or at any rate that it does not decompose into the quinonediazide.

Hantzsch states in his last paper (1) that the primary yellow amorphous product contains *s*-tribromophenylnitrosoamine, since, when treated with alcoholic β-naphthol, *s*-tribromobenzeneazo-β-naphthol is formed, and (2) that the yellow aqueous extract of this solid is a solution of the nitrosoamine; this solution, according to Hantzsch,

gives no precipitate of silver bromide until it is warmed, and consequently the nitrosoamine decomposed, and at first gives merely the ordinary coupling with β-naphthol, and only after heating the characteristic colour of the quinonediazides with this reagent.

The following experiments have been made to throw light on these points.

Investigation of the Decomposition of Sodium s-*Tribromobenzenediazotate by the Addition of Acid.*

A 0·75 per cent. solution of the diazotate was prepared by adding 0·5 gram of the diazonium hydrogen sulphate in 50 c.c. of water to 25 c.c. of a 10 per cent. solution of sodium hydroxide cooled to 0°. The colourless mixture was cooled until it partially froze, the temperature being −1°, obviously the lowest temperature obtainable. A current of carbon dioxide was now passed in until a copious, yellow precipitate was formed. The temperature was then allowed to rise until the whole of the ice had melted; it never exceeded −0·5°. The yellow solid was rapidly collected on an ice-cold filter and washed with ice-cold water. The yellow filtrate was directly received into cooled dilute nitric acid in order to stop the decomposition of the diazo-compound, and the bromide immediately precipitated by silver nitrate, when 0·1688 gram of silver bromide was found, this being equivalent to 79 per cent. of one atomic proportion of bromine.

In the author's first experiments (Trans., 1903, **83**, 808), which were carried out in a cooled solution, 82 per cent. of one atomic proportion of bromine was eliminated. On keeping the filtrate from the silver bromide for 24 hours, no further precipitation of bromide was observed.

The Yellow Solid.—A portion of the yellow solid directly after collection and washing with ice-cold water was suspended in water and kept for 24 hours (temperature, 15—17°). The yellow filtrate thus obtained gave no precipitate with silver nitrate. If the unstable nitrosoamine were present in the yellow solid, then, according to Hantzsch, when treated in this manner, it should have decomposed into the quinonediazide and hydrogen bromide, which should have been recognisable in the solution.

The remainder of the yellow solid was suspended in alcoholic β-naphthol and kept for 24 hours; the orange-coloured liquid was then filtered from yellow solid and cautiously precipitated with water. The very small quantity of red flocks which separated was washed with alcohol, and melted directly at 155—165°. Hantzsch gives 169° as the melting point, but records no analysis of this solid, which he takes to be nearly pure *s*-tribromobenzeneazo-β-naphthol (m. p. 179—180°).

When the aqueous and more especially the alcoholic alkaline solution of this solid (m. p. 165°) was cautiously neutralised, the characteristic colour-changes of the coupled product of a quinonediazide with β-naphthol were observed. The alcoholic extract contains, however, besides the small amount of coupled β-naphthol derivative, a considerable quantity of 3:5-dibromoquinonediazide, which, on adding water, is partially precipitated with the β-naphthol derivative; this no doubt accounts for the low and indistinct melting point, 165°, observed for the red flocks; the dibromophenolazo-β-naphthol melts at 216—217°. The presence of the quinonediazide in the alcoholic solution of the β-naphthol, in which the yellow solid has been suspended, can be very readily demonstrated by adding a drop of sodium hydroxide solution (see p. 104). The characteristic coupling of a quinonediazide begins immediately, and the crystalline product which separates melted directly at 210°. Moreover, the quinonediazide can itself be isolated in a pure and crystalline condition (decomposing at 140°) from the alcoholic solution of β-naphthol used for extraction, by carefully regulated addition of water.

Decomposition of s-*Tribromobenzenediazonium Hydrogen Carbonate.*—Owing to the length of time required for the diazonium acetate to change to an appreciable extent, the hydrogen carbonate was exclusively used in these experiments; it was prepared by adding a slight excess of sodium hydrogen carbonate over the quantity required by the ratio, $(C_6H_2Br_3{\cdot}N_2{\cdot}HSO_4):2(NaHCO_3)$, to the aqueous solution of the diazonium hydrogen sulphate.

A solution of 0·5 gram of the diazonium hydrogen sulphate in 50 c.c. of water was partially frozen, and a solution of 0·2 gram of sodium hydrogen carbonate in 25 c.c. of ice-cold water rapidly added. The ice was allowed to melt and the yellow solid collected on a cooled funnel within 20 minutes of mixing. The filtrate was received into dilute nitric acid and the bromide precipitated.

0·0858 gram of AgBr was found, this being equivalent to 40 per cent. of one atomic proportion of bromine.

In a second experiment, performed in an exactly similar manner, 0·0866 gram of AgBr was found, an amount equivalent to 40·5 per cent. of one atomic proportion of bromine.

In order to ascertain if the yellow solid decomposed on keeping, it was treated, as in the previous experiment, by suspending in water for 24 hours. No bromide was found in the liquid. Moreover, no bromide was formed by boiling some of the yellow solid in water for half an hour.

Another portion was suspended in alcoholic β-naphthol; a small amount of coupling took place, the coupled product behaving as in the last experiment, as the derivative of a quinonediazide; quinonediazide

was also extracted from the yellow solid by the alcoholic β-naphthol, and its presence demonstrated by making the solution alkaline.

It will be noted that in these experiments very small quantities of diazonium hydrogen sulphate were used at any one time. The yellow, amorphous precipitate obtained in the reaction cannot be filtered easily, and is accordingly difficult to wash. Rapidity is essential in dealing with such a substance as the nitrosoamine, which is so sensitive to temperatures above 0°. Further, since the recognition of the nitrosoamine depends mainly on the formation of *s*-tribromobenzeneazo-β-naphthol, it is obvious that all unchanged diazonium salt adhering to the precipitate must be washed away before bringing the solid into contact with the alcoholic β-naphthol.

In the experiment just described, a very dilute (less than 1 per cent.) solution of the diazonium salt was used. In other experiments, more concentrated solutions up to 10 per cent. have been employed, without, however, affecting the results.

It would appear therefore as if the yellow solid, prepared by both methods at the lowest attainable temperature, undergoes on keeping at a higher temperature no decomposition in which hydrogen bromide is eliminated ; further, the yellow solid always contains the quinonediazide.

Behaviour of the Aqueous Extract of the Yellow Solid.—The yellow solid was prepared, as above described, by treating a solution of diazonium hydrogen sulphate (1 gram-mol.) with sodium hydrogen carbonate (2 gram-mols.). The product, the temperature of which was not allowed to rise above 0°, was extracted with 100 c.c. of ice-cold water for half an hour. The yellow solution thus obtained gave no precipitate with silver nitrate ; after boiling, a cloudiness was observed, which disappeared on the addition of nitric acid and could not therefore be a precipitate of silver bromide. It coupled faintly both before and after boiling with β-naphthol. After keeping for 24 hours, its behaviour towards silver nitrate was unchanged. On shaking with chloroform, which entirely extracts the quinonediazide (see p. 104) a colourless liquid remains, showing no sign of coupling and giving no precipitate with silver nitrate. The diazophenol in the chloroform extract was converted into the β-naphthol derivative, which gave directly the correct melting point, 216—217°. The aqueous extract behaved, in fact, exactly as if it were an aqueous solution of 3 : 5-dibromoquinonediazide.

Estimation of the Quinonediazide in the Yellow Solid.—In order to demonstrate as completely as possible that the quinonediazide does not arise from a decomposition in the primary yellow solid, attempts were made to estimate directly the proportion of the diazide present, and at the same time to show that this quinonediazide is not the product

of the decomposition of the nitrosoamine. Since the latter change must be accompanied by the formation of hydrogen bromide, its extent, if it occurs, could be easily measured.

Detection and Estimation of the Quinonediazide.—It is remarkable that in neutral or faintly acid solution (either alcoholic or aqueous), quinonediazides couple very slowly indeed with β-naphthol, but in the presence of a minute quantity of a base, either a hydroxide or such a base as pyridine, the coupling is not only rapid but complete. The best method of coupling a quinonediazide with β-naphthol is to dissolve both substances in alcohol and then add from 0·5 to 1 c.c. of 0·5 per cent. solution of sodium hydroxide. Coupling begins immediately, the solution acquiring a characteristic purple colour. In a short time, crystals of the coupled product appear, and the process is complete in 3 or 4 hours, although when the quinonediazide was to be estimated the mixture was left overnight; it was then acidified with a drop of acetic acid and the solid collected on a Gooch filter, washed with alcohol, dried at 100°, and weighed. In order to estimate the quinonediazide in aqueous solution, the liquid was extracted three times with chloroform, which removed the diazide completely, leaving a colourless solution; the chloroform was evaporated at a low temperature, and the residue taken up in alcohol, in which the coupling was carried out. When the quinonediazide has to be extracted from a solution containing diazonium salt, the chloroform must be very carefully separated from the aqueous liquor. Solids containing a quinonediazide can be extracted directly with cold alcohol.

Comparative experiments were made with *p*-nitrophenylnitrosoamine, $NO_2\cdot C_6H_4\cdot NH\cdot NO$, which was prepared according to Schraube and Schmidt's directions (*Ber.*, 1894, **27**, 518). In alcoholic solution, the nitrosoamine couples very rapidly with β-naphthol; the reaction does not appear either to be accelerated by the presence of bases or to be rendered more complete. This nitrosoamine therefore offers a marked contrast to the quinonediazides in this respect.

In the estimation of the quinonediazide in the original yellow solid by conversion into the β-naphthol derivative, the formation of hydrogen bromide during the operation was carefully looked for. The yellow solid for each experiment was prepared from 2 grams of *s*-tribromobenzenediazonium hydrogen sulphate, which was dissolved in 25 c.c. of water, the solution partially frozen, and then 0·8 gram of sodium hydrogen carbonate (2·1 equivalents) dissolved n 25 c.c. of ice-cold water added. The ice in the mixture was allowed to melt, the temperature never rising above 0°. The yellow solid was rapidly collected and washed with ice-cold water. The filtrate contained bromide equivalent to 41 per cent. of one atomic proportion of bromine. The solid was left in contact with 75 c.c. of ice-cold alcohol for half an

hour; the yellow solution was filtered and 1 gram of β-naphthol in 15 c.c. of cold alcohol added. On introducing 0·005 gram of sodium hydroxide dissolved in 1 c.c. of water, a rapid coupling immediately began. After 24 hours, the deeply-coloured liquid from which crystals had separated was acidified with acetic acid and the solid dibromophenolazo-β-naphthol collected, washed with alcohol, and weighed. The weight was 0·24 gram, and the substance melted without recrystallisation at 213° instead of 216°. This amount of coupled quinonediazide represents 12·5 per cent. of the diazonium salt used. The amount of quinonediazide does not correspond to the bromine eliminated, since not only does a portion remain in the aqueous liquor, but also part condenses forming the yellow amorphous powder.

If the whole of the quinonediazide found was not originally present in the yellow solid, but was formed secondarily from the nitrosoamine during the treatment with cold alcohol, or after addition of sodium hydroxide, then not only should hydrobromic acid have been formed, thus neutralising the alkali (0·005 gram NaOH), but bromine ions should have been found in the alcoholic liquor. The liquid, however, remained alkaline during the 24 hours through which it was kept for the coupling to become complete. Finally, the bromide was estimated in the alcoholic mother liquor, from which the coupled product had been filtered. The liquor was poured into 500 c.c. of water, kept for 24 hours, and the β-naphthol filtered off. Silver nitrate and nitric acid were then added; a slight red precipitate was formed, which was collected in a weighed Gooch crucible and there washed with alcohol and finally with ether. No solid remained in the crucible, the weight of which, after drying at 150°, was unchanged. If the quinonediazide which was found had been entirely formed from nitrosoamine, originally present in the yellow solid, 0·107 gram of silver bromide would have been obtained.

Repetitions of this experiment gave exactly similar results, 0·23 gram and 0·232 gram respectively of coupled product being found and no silver bromide obtained from the alcoholic filtrate.

In another experiment, the conditions were somewhat varied; 3 instead of 2·1 equivalents of sodium hydrogen carbonate were used, and the mixture was only allowed to stand for 15 minutes. Fifty per cent. of one atomic proportion of bromine was found in the aqueous filtrate. The alcoholic extract of the yellow solid yielded dibromophenolazo-β-naphthol, representing 12·07 per cent. of the diazonium salt used.

It will be seen therefore from the above experiments that not only has it been impossible to obtain any evidence of the presence of the nitrosoamine in the yellow solid formed in the decomposition of *s*-tribromobenzenediazonium salts of weak acids (hydrogen carbonates), but it seems impossible to doubt that the quinonediazide, which can be

recognised and estimated in the yellow solid, is not produced even partly from the nitrosoamine originally present therein, since the other product of the decomposition, hydrogen bromide, cannot be found.

Up to the present the author has not been able to obtain any evidence of the formation of the nitrosoamine; under the conditions when its formation, from analogy with the formation of Schraube and Schmidt's *p*-nitrophenylnitrosoamine, was to be expected, another reaction takes place, namely, the displacement of bromine by hydroxyl, a reaction which is not possible in the case of the *p*-nitro-derivative.

It will be convenient here to record some experiments on the decomposition of *s*-tribromobenzenediazonium salts in the presence of a hydrogen carbonate; these experiments bear on the results given in the first part of this paper, and illustrate the effect of the proportion of hydrogen carbonate and of time and temperature on the extent of the reaction.

The reaction between the diazonium hydrogen sulphate and the hydrogen carbonate never leads (at the ordinary temperature) to the complete elimination of one atomic proportion of bromine, owing to the condensation of the undecomposed diazo-compound both with itself and with the quinonediazide; the condensation product is the yellow, amorphous, insoluble powder of high molecular weight, which generally forms the major part of the yellow precipitate. The following table shows the effect of the proportion of hydrogen carbonate on the extent of the reaction.

For each gram-mol. of diazonium hydrogen sulphate, the following quantities of hydrogen carbonate were used:

Gram-mols. of hydrogen carbonate	2	3	4	8
Percentage of one atomic proportion of bromine, appearing as bromine ions	49	55	81	87

When two gram-mols. of hydrogen carbonate are used, it will be noticed that the reaction ceases (practically) when sufficient bromine ions have been produced to convert completely any hydrogen carbonate into bromide.

The effect of time is shown in the following results:

Gram-mols. of hydrogen carbonate for 1 gram-mol. of diazonium salt.	Time occupied by the reaction.	Percentage of one atomic proportion of bromine, found as ions.
2	10 minutes	40
2	1·75 hours	41
2	72 ,,	49
4	2 ,,	81
4	772 ,,	81
8	15 minutes	86
8	72 hours	87

The effect of temperature between the limits of 0° and 15° is very small. Thus, using 4 gram-mols. of hydrogen carbonate (time, 2 hours), 79·4 per cent. of one atomic proportion of bromine was eliminated at 0°, whilst at 13° 81 per cent. was found.

From this result, it appears that the difference between the author's and Hantzsch's results is not due to the difference of temperature at which the reactions were carried out.

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XV.—*The Determination of Acetyl Groups.*

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FOR the estimation of acetyl groups in the acetyl derivatives of phenolic substances, the indirect method which consists in the determination of the percentage of regenerated phenol given by hydrolysis is, when available, the most advantageous. The employment of sulphuric acid for this purpose appears to have been first described by Liebermann (*Ber.*, 1884, **17**, 1682), who analysed acetylquercetin by means of a 70 per cent. acid at the temperature of the water-bath. Various modifications of this method have been employed by others, and I have shown that hydrolysis with sulphuric acid in the presence of acetic acid (1 gram of substance, 15 c.c. of acetic acid, and 2 c.c. of sulphuric acid approximately) at the boiling heat gives good results with most acetyl compounds (Trans., 1896, **69**, 210). The product of the reaction, on cautious dilution with boiling water, as a rule, deposits the phenol in a crystalline condition, and the substance is thus very easily collected and washed. This method has also been employed with a satisfactory result at the ordinary temperature (Trans., 1898, **74**, 1034), and again the sulphuric acid can be replaced by hydrochloric acid (5 c.c.) when sulphonation is likely to occur (Trans., 1899, **75**, 448). Alkaline hydrolytic agents are sometimes serviceable as regards the indirect method, but in cases where the regenerated phenol is liable to attack by the alkali, strong alcoholic potassium acetate can frequently be employed with advantage.

In many cases, however, the indirect method is not available, and it

is then necessary to determine the acetic acid produced by the hydrolysis. For this purpose, the decomposition of the acetyl compound is effected by means of potassium hydroxide, barium hydroxide (Herzig, *Monatsh.*, 1884, **5**, 86), magnesia (Schiff, *Ber.*, 1879, **12**, 1531), &c., and the acetic acid estimated in various ways. The latter reagents have been employed in certain cases where a strong alkali would react on the phenol itself; for instance, according to Erdmann and Schultz (*Ann.*, 1882, **216**, 234), acetylhæmatoxylin evolves formic acid when digested with boiling dilute alkali. F. Wenzel (*Monatsh.*, 1897, **18**, 659) prefers to hydrolyse the substance with a slightly diluted sulphuric acid, sodium phosphate being then added and the acetic acid distilled off under reduced pressure. Such processes, however, involve, as a rule, long and tedious operations, and are not always reliable with small quantities of substance, and it was consequently interesting to determine whether some simpler and more rapid method could not be devised.

It was previously found (Trans., 1899, **75**, 433) that the acetyl derivatives of phenolic colouring matters are hydrolysed by boiling alcoholic potassium acetate solution with the production of ethyl acetate and the mono- and di-potassium salts of the substance, and experiments with other *O*-acetyl compounds showed that in all cases ethyl acetate was evolved by this method. In order to study the process, 0·5 gram of the substance was digested at the boiling temperature in a small retort with a half-saturated solution of potassium acetate in alcohol for one and a half hours, the volume of the liquid being made up from time to time with fresh quantities of alcohol. The distillate was treated with standard alcoholic potash, heated to boiling to saponify the ethyl acetate present, and titrated with sulphuric acid to determine the quantity of acetic acid which was thus produced. The earlier experiments carried out in this manner gave satisfactory results, as acetylbutin, $C_{15}H_9O_5(C_2H_3O)_3$, yielded 45·60 per cent. of acetic acid (theory, 45·23 per cent.), and acetylbutein, $C_{15}H_8O_5(C_2H_3O)_4$, 54 per cent. (theory, 54·54 per cent.), but with some other compounds the reaction proceeded but slowly and involved the use of large quantities of alcohol. For instance, penta-acetylcatechin, $C_{15}H_9O_6(C_2H_3O)_5$ (m. p. 129—130°), was not completely hydrolysed after 3 hours' digestion with the acetate (found, acetic acid = 43·35; theory requires 60 per cent.), and a somewhat similar result was given by acetylcyanomaclurin, $C_{15}H_9O_6(C_2H_3O)_5$ (found, 35·8; theory requires 60 per cent.). Although it appeared quite possible by a longer treatment, or the employment of a higher temperature, to devise a method by which the use of potassium acetate would be generally applicable, the experiments were not continued, as the following process, in which the acetate is replaced by sulphuric acid, gave satisfactory and rapid results.

In carrying out this operation, 0·5 gram of the substance (approx.), 30 c.c. of alcohol, and 2 c.c. of sulphuric acid are placed in a small retort and the mixture gently distilled until about one-third of its bulk remains. Twenty c.c. of fresh alcohol are then added, the operation repeated, and a second, and sometimes a third, quantity of the alcohol run in. The distillate is collected in a flask containing 20 c.c. of standard alcoholic potash solution, and at the end of the operation is connected to a reflux condenser and heated on the water-bath for a few minutes. The product diluted with a little water is titrated with standard sulphuric acid.* It has been usual to distil slowly so that about three-quarters of an hour is thus occupied, and it is of course necessary that the distillation be not carried too far, otherwise an evolution of sulphurous acid will thus occur. In order that no traces of acid liquid can be carried over by spurting, the tubulure of the retort is bent from the centre at a slight angle, and into the neck a small tap funnel is fitted by means of which the fresh alcohol is added during the distillation. The whole operation should not require more than an hour and a quarter, and less than this is usually sufficient. The following acetyl derivatives, specially prepared, have been analysed by this method.

		Acetic acid.	
		Found.	Theory.
Acetylalizarine	$C_{14}H_6O_4(C_2H_3O)_2$	37·59	37·04
Acetylquercetin	$C_{15}H_5O_7(C_2H_3O)_5$	58·44	58·59
Acetylpurpurogallin	$C_{11}H_4O_5(C_2H_3O)_4$	62·40	61·86
Acetylbutin	$C_{15}H_9O_5(C_2H_3O)_3$	{ 45·60 / 45·34 }	45·23
Acetylcatechin (m. p. 129—130°)	$C_{15}H_9O_6(C_2H_3O)_5$	60·24	60·00
Acetylcatechin (m. p. 158—160°)	$C_{15}H_9O_6(C_2H_3O)_5$	60·18	60·00
Acetylhesperitin	$C_{16}H_{11}O_6(C_2H_3O)_3$	42·54	42·06

It was found possible, except in the case of the catechins, to recover the phenolic compounds regenerated by the reaction in a pure condition, and it is quite evident that where these substances are insoluble in cold water an indirect determination can be simultaneously carried out by this method. The above results require no special comment, though it is interesting to observe that acetylhesperitin has given numbers in harmony with those previously obtained by hydrolysis in the cold (Trans., 1898, **74**, 1034). Various other *O*-acetyl compounds have been analysed by this method with good result, and these will be referred to in later communications.

It is possible that the sulphuric acid in this process can be replaced by phosphoric acid. In one experiment with diacetylalizarine an acid of 1·5 sp. gr. gave, during an hour and a half, 17·8 per cent. of acetic

* Normal sulphuric acid was usually employed, but when only small quantities of substance are available, a more dilute acid is preferable.

acid (theory 37·59) as ethyl acetate, and it seems likely that had the reagent been stronger a more satisfactory result could thus have been obtained.

Acetylamido-compounds.

The method described is also applicable to *N*-acetyl derivatives, but in this case is not so important, because the detection of amido-groups can be so readily effected by the well known "nitrite" process. For these determinations, 4 c.c. of sulphuric acid in 30 c.c. of alcohol have been usually employed, and the solution was concentrated during the operation to at least one-third its bulk, for hydrolysis with these compounds does not proceed so readily as with the *O*-acetyl derivatives. The residual liquid is diluted with alcohol and the mixture distilled as before, and this is repeated until the distillate is free from ethyl acetate. The reaction is usually complete in an hour and a half, and the only precaution necessary is to observe that the concentration does not proceed too far. The following results were obtained with products specially prepared for the purpose:

		Acetic acid.	
		Found.	Theory.
Acetanilide	$C_6H_5 \cdot NH \cdot CO \cdot CH_3$	{44·74, 44·55}	44·44
Aceto-*p*-toluidide	$C_7H_7 \cdot NH \cdot CO \cdot CH_3$	39·85	40·21
Diacetylbenzidine	$C_{12}H_8(NH \cdot CO \cdot CH_3)_2$	44·54	44·77

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XVI.—*Studies in the Camphane Series. Part XVI. Camphorylcarbimide and Isomeric Camphorylcarbamides.*

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THE readiness with which bornylamine, the amino-derivative of a fully hydrogenated cycloid, is converted into bornylcarbimide by the action of nitrous acid on the carbamide (Forster and Attwell, Trans., 1904, **85**, 1188) has led us to examine the behaviour of more complex bases from the same standpoint. Choosing aminocamphor as a convenient type of the amino-ketones, we treated the hydrochloride with potassium cyanate in order to prepare the camphorylcarbamide obtained by Rupe (*Ber.*, 1894, **27**, 584, and 1895, **28**, 778), and at this stage encountered circumstances which have brought to light a camphoryl-ψ-carbamide exhibiting interesting properties.

Rupe describes the carbamide of aminocamphor as melting at 169° without evolving gas, and yielding with condensing agents camphorimidazolone, $C_{11}H_{16}ON_2$, infusible at 320°; nitrous acid transformed his modification of camphorylcarbamide into a compound melting at 77°, the properties of which escaped examination, whilst the substance itself was not analysed.

Although we substantiate Rupe's account in every particular, our experiments show that a very slight modification of his conditions leads to an isomeric substance which melts somewhat indefinitely and decomposes at 184°, and yields with nitrous acid at 0° a true nitroso-derivative melting at 158°. The new compound, however, resembles Rupe's in furnishing camphorimidazolone when dissolved in concentrated sulphuric acid, and if treated with nitrous acid in the absence of precaution against rise of temperature, it gives the substance melting at 77° which was obtained by Rupe from his camphorylcarbamide; moreover, the differences in solubility, and in specific rotatory power, displayed by the two isomerides, are unimportant.

At first we suspected the discrepancy between Rupe's results and our own to depend upon a difference in the specimens of aminocamphor employed, because Rupe prepared his material by reducing *iso*nitrosocamphor with zinc and acetic acid, whereas we applied the alkaline method, and in working with substitution products of camphor it is necessary to keep in view the possible occurrence of *cistrans*-isomerism, as in the case of bornylamine and neobornylamine. We find, however, that the formation of the isomeric camphorylcarbamides does not depend upon the source of the aminocamphor, but is influenced by the concentration of the liquid in which the hydrochloride of the base interacts with potassium cyanate, and by the presence of acid or alkali.

The production of two carbamide derivatives from a single base is a somewhat unusual occurrence, and the distinction offered by aminocamphor in this respect from bornylamine and aniline, each of which yields one carbamide only, appears to indicate the carbonyl group as causing the divergence of behaviour.

On considering the possible constitution of the two isomerides, numerous structural formulæ suggest themselves.

I. $C_8H_{14}<\begin{array}{l}CH\cdot NH\cdot CO\cdot NH_2\\ |\\ CO\end{array}$ II. $C_8H_{14}<\begin{array}{l}CH\cdot N{:}C(OH)\cdot NH_2\\ |\\ CO\end{array}$

II*a*. $C_8H_{14}<\begin{array}{l}CH\cdot NH\cdot C(OH){:}NH\\ |\\ CO\end{array}$ III. $C_8H_{14}<\begin{array}{l}CH\text{——}NH\\ |\\ C(OH)\cdot NH\end{array}>CO$

IV. $C_8H_{14}<\begin{array}{l}CH\text{—}NH\\ |\\ C(OH)\text{—}N\end{array}\geqslant C\cdot OH$ V. $C_8H_{14}<\begin{array}{l}CH\text{—}NH\\ |\\ C(OH)\text{—}O\end{array}>C{:}NH$

VI. $C_8H_{14}<\begin{array}{l}CH\text{——}N\\ |\\ C(OH)\cdot O\end{array}\geqslant C\cdot NH_2.$

Of these expressions, II with II*a*, IV, and VI are the tautomeric forms of I, III, and V, respectively, and although there can be little doubt that one or other of the compounds has the normal structure I, it is not easy to draw a definite conclusion regarding the isomeride; before doing so it will be necessary to indicate briefly the various properties which must be brought into agreement.

It has been mentioned that the substance melting at 77°, obtained by Rupe from camphorylcarbamide and nitrous acid, was not further examined by its discoverer; on preparing it for comparison with the nitroso-derivative of camphoryl-ψ-carbamide, we found that it is the hitherto unknown camphorylcarbimide, $C_8H_{14}<\begin{matrix}CH\cdot N:C:O\\ |\\ CO\end{matrix}$. Not only does this compound arise from the *pseudo*-carbamide also if the action of nitrous acid is not controlled by a low temperature, but it is produced immediately, with liberation of nitrogen, when the freshly prepared camphorylnitroso-ψ-carbamide is warmed with water; if, however, the nitroso-compound is dried in the desiccator, or recrystallised from alcohol, boiling water has no action upon it. The behaviour of the two carbamides towards nitrous acid appears to differ, therefore, in the fact that a hydrated nitroso-derivative, forming an intermediate stage in the production of the carbimide, can be isolated only in the case of the *pseudo*carbamide.

Towards hydroxylamine acetate they behave alike. With this agent, both yield the oxime of camphorylcarbamide, $C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CO\cdot NH_2\\ |\\ C:NOH\end{matrix}$, obtained from α-aminocamphoroxime hydrochloride and potassium cyanate by Lapworth and Harvey (Trans., 1902, **81**, 553). Here again, the production of a single oxime from the two carbamides indicates the carbonyl group as the cause of isomerism, which disappears with oximation of the ketone.

If the hydrochloride of methylaminocamphor is treated with potassium cyanate, two carbamides again are formed. One of these has been described already by Duden and Pritzkow (*Ber.*, 1899, **32**, 1538) as melting at 185°; in addition to this compound we have obtained a *pseudo*-carbamide melting at 200°, and, as would be foreseen from the position of the methyl group, nitrous acid is without action on either compound. Of the two pairs of carbamides which have been studied, the one of lower melting point is transformed into the *pseudo*-modification by aqueous alkalis, whilst dilute acids bring about the converse change.

The foregoing facts lead us to regard Rupe's carbamide as having the normal structure I, and to represent the *pseudo*-modification by formula III. Expressions corresponding with V and VI have been used by Gabriel (*Ber.*, 1889, **22**, 2990; compare also Hirsch, *Ber.*, 1890, **23**,

966, Gabriel and Stelzner, *Ber.*, 1895, 28, 2929) in explaining the transformation of allylcarbamide into propylene-ψ-carbamide, which is obtained also from β-bromopropylamine hydrobromide and potassium cyanate, but these do not appear to us applicable in the present instance, chiefly owing to the difficulty of eliminating ammonia by alkalis, and to the readiness with which camphorimidazolone,

$$C_8H_{14}<\begin{array}{l}CH\cdot NH\\ \vert \\ C{=\!=\!=}N\end{array}>CO,$$

is obtainable by the action of dehydrating agents.

By analogy with the camphorylcarbamides, the camphorylmethylcarbamide described by Duden and Pritzkow, and the *pseudo*-modification mentioned above, will be represented by the formulæ

$$C_8H_{14}<\begin{array}{l}CH\cdot NMe\cdot CO\cdot NH_2\\ \vert \\ CO\end{array} \quad \text{and} \quad C_8H_{14}<\begin{array}{l}CH{-\!-}NMe\\ \vert \\ C(OH)\cdot NH\end{array}>CO$$

respectively, whilst the indifference of these compounds towards nitrous acid indicates the structure $C_8H_{14}<\begin{array}{l}CH\cdot N(NO)\\ \vert \\ C(OH)\cdot NH\end{array}>CO$ for the nitroso-derivative of camphoryl-ψ-carbamide. The decomposition of the last-named substance in its hydrated form when warmed with water is explained by the equation

$$C_8H_{14}<\begin{array}{l}CH{-\!-\!-}N{-\!-\!-}\\ \vert \quad HO{-}N{-}OH\\ \quad OH\\ C{-\!-\!-}NH{-\!-\!-}\end{array}>CO = C_8H_{14}<\begin{array}{l}CH\cdot N{:}C{:}O\\ \vert \\ CO\end{array} + N_2 + 2H_2O.$$

From a study of camphorylthiocarbamide and the carbamino-derivatives of the camphylamines, we hope to gain further information respecting this case of isomerism, and are therefore continuing the investigation on these lines.

It remains to be stated that camphorylcarbimide closely resembles bornylcarbimide in general properties; it surpasses that substance in chemical activity, however, being converted into the disubstituted carbamide much more readily by water, and yielding with methyl and ethyl alcohols the corresponding carbamates. From this point of view, therefore, it lies between bornylcarbimide and phenylcarbimide.

EXPERIMENTAL.

Camphoryl-ψ-carbamide, $C_8H_{14}<\begin{array}{l}CH{-\!-\!-}NH\\ \vert \\ C(OH)\cdot NH\end{array}>CO.$

Fifty grams of *iso*nitrosocamphor dissolved in 200 c.c. of water containing 60 grams of sodium hydroxide were treated with 50 grams of zinc dust, the liquid being vigorously shaken and cooled. The

precipitated aminocamphor was removed by means of ether, dissolved in 80 c.c. of 15 per cent. hydrochloric acid, and mixed with 50 grams of potassium cyanate in 150 c.c of water. A viscous oil was immediately precipitated, and after 15 minutes the product was rendered alkaline with a 20 per cent. solution of sodium hydroxide, which transformed the oil into a crystalline paste in the course of 1 hour. The filtered substance was recrystallised from boiling water, concentrated solutions depositing leaflets, whilst needles separated from the diluted liquid; the specimen for analysis was further crystallised from benzene mixed with a small proportion of absolute alcohol, being thus obtained in felted masses of silky white needles which retained the solvent with such tenacity that until the substance had been heated for some time at 90°, the percentage of carbon was systematically higher than that indicated by theory.

0·1311 gave 0·3016 CO_2 and 0·1015 H_2O. C = 62·75; H = 8·66.
0·0990 „ 12·0 c.c. of nitrogen at 25° and 758 mm. N = 13·50.
$C_{11}H_{18}O_2N_2$ requires C = 62·86; H = 8·57; N = 13·33 per cent.

The melting point is somewhat indefinite, as the compound evolves gas, but fusion generally occurs at 184°, although one specimen crystallised from water melted at 188°. It is insoluble in boiling light petroleum, but is readily soluble in cold chloroform and absolute alcohol; warm ethyl acetate also dissolves it readily, but less freely than the isomeric carbamide, whilst warm acetone, in which it dissolves without difficulty, deposits it in well formed, rectangular plates, distinct from the silky needles in which camphorylcarbamide is deposited by the same medium. A solution containing 0·4609 gram in 25 c.c. of absolute alcohol gave $\alpha_D - 30'$ in a 2-dcm. tube, whence $[\alpha]_D - 13·5°$.

Camphoryl-ψ-carbamide does not lose ammonia when boiled with 40 per cent. potassium hydroxide, but it is rapidly changed by concentrated sulphuric acid, yielding camphorimidazolone, which dissolves with difficulty in boiling alcohol, crystallising in lustrous needles infusible at 300°. The most satisfactory process for obtaining this compound is to dissolve 1 gram of the *pseudo*-carbamide in 2 c.c. of concentrated acid, heat in steam during 1 minute, and dilute largely with water; if the action is protracted, the colour of the liquid changes through pale red and intense reddish-brown to deep greenish-purple, finally acquiring the appearance of malachite green. These colour transformations are associated with the gradual destruction of the imidazolone.

Action of Hydroxylamine Acetate.—Two grams of the *pseudo*-carbamide were dissolved in 20 c.c. of absolute alcohol and heated with 4 grams of hydroxylamine hydrochloride and 10 grams of sodium acetate during 6 hours; on pouring the product into water, lustrous leaflets were

precipitated, crystallising from water in transparent, hexagonal plates. The oxime melts and decomposes at 202—203°, and appears to be identical with the carbamide obtained by Lapworth and Harvey from α-aminocamphoroxime (Trans., 1902, 81, 553).

In order to compare camphoryl-ψ-carbamide with Rupe's derivative, we prepared the latter by dissolving 10 grams of α-aminocamphor carbonate in 150 c.c. of 2 per cent. hydrochloric acid, and treating the filtered liquid with 10 grams of potassium cyanate; the filtrate remained clear during 24 hours, when long needles began to separate, and gradually filled the solution. The product, when completely dry, dissolved readily in cold benzene, but immediately separated in a voluminous mass of silky needles; this behaviour is doubtless due to assimilation of benzene of crystallisation, because the air-dried crystals require to be exposed to a temperature of 80° during a considerable period before the odour of the hydrocarbon is removed. In this respect the normal carbamide resembles the *pseudo*-modification, and with the exception already mentioned, the behaviour of the two substances towards solvents generally is exactly similar. Moreover, the colour-changes undergone by a solution of the carbamide in concentrated sulphuric acid on heating are identical with those recorded in connection with the *pseudo*-carbamide, and the oxime described above is obtained when the carbamide is heated with hydroxylamine acetate. Rupe's compound melts at 169°, and a solution containing 0·5275 gram in 25 c.c. of absolute alcohol gave α_D 18′ in a 2-dcm. tube, whence $[\alpha]_D + 7{\cdot}1°$.

In describing the production of this compound, Rupe (*Ber.*, 1895, 28, 778) mentions the formation of an oil when aminocamphor hydrochloride dissolved in water is warmed with potassium cyanate, and states that great difficulty was experienced in causing it to become crystalline. In the light of our experiments, it appeared probable that this oil was a mixture of camphoryl-ψ-carbamide with the normal compound, and having found that alkali facilitated its solidification, we proceeded to examine the behaviour of Rupe's carbamide towards alkali; 1 gram of the finely powdered substance was agitated with 10 per cent. sodium hydroxide during 2 hours, when the product was found to consist of the *pseudo*-carbamide. The converse change is brought about by dilute acids, a specimen of camphoryl-ψ-carbamide, when left in contact with dilute hydrochloric acid, and shaken at intervals during several days, changing completely into Rupe's compound.

Camphorylnitroso-ψ-carbamide, $C_8H_{14}<\begin{matrix}CH\cdot N(NO)\\ |\\ C(OH)\text{-}NH\end{matrix}>CO.$

Twenty grams of camphoryl-ψ-carbamide were suspended in 1 litre of water, treated with 60 c.c. of concentrated hydrochloric acid in 150 c.c. of water, and cooled by the addition of crushed ice; 20 grams of solid sodium nitrite were then added slowly, the liquid being stirred vigorously during the operation. After half an hour, the bulky, pale yellow precipitate was filtered, washed, dried in the desiccator, and subsequently crystallised from alcohol, separating in lustrous, pale yellow needles; when newly withdrawn from the mother liquor, it melts and decomposes at 142°, but after some days the crystals become opaque and melt at 158°.

0·1433 gave 0·2874 CO_2 and 0·0960 H_2O. C = 55·08; H = 7·44.
0·2170 „ 33·6 c.c. of nitrogen at 25° and 760 mm. N = 17·30.
$C_{11}H_{17}O_3N_3$ requires C = 55·23; H = 7·16; N = 17·57 per cent.

A solution containing 0·3138 gram dissolved in 25 c.c. of chloroform gave α_D 4° 15′ in a 2-dcm. tube, whence $[\alpha]_D + 169·3°$.

The nitroso-derivative is insoluble in boiling light petroleum, and only sparingly soluble in benzene, from which it crystallises in silky needles; chloroform, ethyl acetate, and acetone dissolve it freely. It gives the Liebermann reaction with all the stages well defined, and does not reduce Fehling's solution on boiling.

In preparing the compound by the above process it is of the greatest importance to keep the liquid within a few degrees of zero, and to add the nitrite very slowly; if these precautions are not observed, nitrogen is evolved briskly, and the product consists of camphorylcarbimide (see below). It appears that the tendency to produce this substance is great, because even the nitroso-derivative, when freshly prepared, and while still wet, yields the carbimide on treatment with hot water; for this reason it is necessary to dry the substance thoroughly in the desiccator before attempting to recrystallise it.

When the nitroso-derivative is treated with cold concentrated aqueous caustic potash, a very vigorous action occurs, nitrogen is liberated, and an oil produced which recalls the odour of geranium; we are still investigating this change, and find that the production of an acidic substance free from nitrogen is accompanied by elimination of cyanic acid. The reduction of the compound has also given interesting results, which we hope to communicate shortly.

Camphorylmethyl-ψ-carbamide, $C_8H_{14}<\begin{matrix}CH—NMe\\ \vert \\ C(OH)\cdot NH\end{matrix}>CO$.

Twenty grams of methylaminocamphor prepared by reducing the nitrogen methyl ether of *iso*nitrosocamphor with zinc and acetic acid (Forster, Trans., 1904, **85**, 898) were dissolved in 50 c.c. of 15 per cent. hydrochloric acid, and slowly treated with 30 grams of potassium cyanate dissolved in 50 c.c. of water; at first the liquid effervesced vigorously and remained clear, but when about half the salt had been added, a viscous oil separated. After an interval of 5 minutes, 10 per cent. sodium hydroxide was added, causing the oil to solidify rapidly, yielding a crystalline product which weighed 20 grams. The compound is sparingly soluble in boiling water, from which it crystallises in lustrous, prismatic needles, or brilliant leaflets, according to the concentration; it melts and evolves gas at 200°.

0·1639 gave 0·3846 CO_2 and 0·1360 H_2O. C = 64·00; H = 9·22.
$C_{12}H_{20}O_2N_2$ requires C = 64·28; H = 8·99 per cent.

A solution containing 0·8155 gram in 25 c.c. of absolute alcohol gave α_D 27′ in a 2-dcm. tube, whence $[\alpha]_D$ +6·9°. The compound is very sparingly soluble in boiling light petroleum, but dissolves readily in hot benzene, crystallising in refractive, clear cut prisms; it is moderately soluble in cold ethyl acetate and acetone, crystallising from both in slender, prismatic needles. Absolute alcohol dissolves it readily, and the solution gives no precipitate with ammoniacal silver nitrate, but on boiling the liquid, reduction takes place slowly. The methyl-ψ-carbamide becomes yellow when boiled with 10 per cent. potassium hydroxide, but ammonia is not evolved; on boiling with Fehling's solution it remains unchanged. The substance distinguishes itself from camphoryl-ψ-carbamide by its indifference towards hydroxylamine acetate, and by its failure to yield a nitroso-derivative.

Action of Sulphuric Acid.—Camphorylmethyl-ψ-carbamide dissolves in hot dilute sulphuric acid, and in the cold concentrated acid with slight rise of temperature. If the latter solution is heated during several minutes in boiling water, the colour deepens from yellow to orange, pale red, intense brownish-red, and finally rich purplish-blue, resembling at this stage the colour developed by ferric chloride with enols. On dilution with water, the liquid yields no precipitate, but develops a green coloration, sufficiently intense at the later stages to recall malachite green. Wool is dyed in a green shade from this acid solution, but the colour produced is not permanent on washing, either with distilled or tap water; the fibre, however, retains a pale brown hue, the green colour being quickly

restored in its original intensity by soaking in dilute mineral acid, but not by acetic acid. If the deep green liquid is rendered alkaline, a pale brown solution is formed, in which acids develop the green colour; the chromophore is therefore amphoteric, and it is not extracted by ether from its solutions in acids and alkalis.

This description of camphorylmethyl-ψ-carbamide distinguishes the substance from the carbamide derivative prepared by Duden and Pritzkow (*Ber.*, 1899, 32, 1542); these authors give no details relating to their method of preparation, but by the action of potassium cyanate on the hydrochloride of methylaminocamphor under the conditions favourable to the production of Rupe's camphorylcarbamide from aminocamphor, we have obtained the compound described by Duden and Pritzkow. Twenty grams of methylaminocamphor dissolved in 300 c.c. of 2 per cent. hydrochloric acid were treated with 25 grams of potassium cyanate in 50 c.c. of water; after half an hour, the filtered liquid began to deposit colourless crystals, the product, after 12 hours, weighing 17·5 grams. It crystallises from benzene in needles which retain the solvent with great tenacity, and, if previously heated for some time at 80° to remove benzene of crystallisation, it melts at 189°, evolving gas (Duden and Pritzkow give 185°). A solution containing 0·4823 gram in 25 c.c. of chloroform gave α_D −58′ in a 2-dcm. tube, whence $[\alpha]_D$ −20·0°.

The two isomerides thus revealed behave alike towards ammoniacal silver nitrate and Fehling's solutions, and a very close examination is required to disclose differences in their solubility relations. Moreover, camphorylmethylcarbamide resembles the *pseudo*-modification in its indifference towards nitrous acid and by its failure to yield an oxime; the changes occurring in the colour of a solution in concentrated sulphuric acid correspond exactly with those displayed by the isomeride.

It has been mentioned that dilute sodium hydroxide transforms the camphorylcarbamide described by Rupe into the isomeric substance prepared by us, and we find that the two camphorylmethylcarbamides are related in the same fashion. One gram of Duden and Pritzkow's carbamide (m. p. 189°) was suspended in 10 per cent. sodium hydroxide, and shaken from time to time during 4 days; the product was then filtered, washed, and recrystallised from benzene, when it melted at 200°.

Camphorylcarbimide (*Camphoryl* iso*Cyanate*), $C_8H_{14}<\begin{matrix}CH\cdot N:C:O\\ |\\ CO\end{matrix}$.

Twenty-five grams of Rupe's camphorylcarbamide were treated with nitrous acid under the conditions described for the preparation of camphorylnitroso-ψ-carbamide; brisk evolution of nitrogen took place, and addition of nitrite was continued until nitric oxide was liberated,

a white precipitate separating gradually. After an interval, this was filtered, washed, and dried in the desiccator. Some difficulty was experienced in purifying the compound, because it is very freely soluble in organic media, and very sensitive to the action of water. Bornylcarbimide can be distilled in steam without undergoing conversion into dibornylcarbamide to an extent greater than 10 per cent., but camphorylcarbimide, although readily volatile, changes quickly into dicamphorylcarbamide when treated with boiling water. Moreover, when the substance is warmed with alcohol, a very vigorous action takes place, but by dissolving it in cold absolute alcohol, diluting this with water, and filtering without delay the crystals which separate during the next few minutes, the carbimide may be obtained in silky, white needles melting at 77°.

0·1782 gave 0·4458 CO_2 and 0·1255 H_2O. C = 68·22; H = 7·87.
$C_{11}H_{15}O_2N$ requires C = 68·39; H = 7·77 per cent.

A solution containing 0·4745 gram in 25 c.c. of chloroform gave α_D −4°51′ in a 2-dcm. tube, whence $[\alpha]_D$ −124·5°.

The carbimide may be obtained also by warming freshly prepared moist camphorylnitroso-ψ-carbamide with water, and even direct from the *pseudo*-carbamide by the action of nitrous acid if the operation is conducted without a liberal supply of ice. An attempt to prepare a nitroso-derivative of the oxime obtainable from the isomeric camphorylcarbamides also gave rise to the carbimide. The oxime suspended in dilute hydrochloric acid was cooled with ice, and treated with its own weight of solid nitrite, which immediately developed a bright blue coloration; this is doubtless due to an unstable nitroso-derivative, because the filtrate from camphorylcarbimide quickly became turbid, lost its colour, and deposited a further quantity of the *iso*cyanate, which is easily recognised by the intense, stupefying odour perceptible on warming the substance with water.

Camphorylcarbimide reacts most vigorously with organic bases, usually forming well-defined carbamides; in the case of aniline and phenylhydrazine, however, although action undoubtedly occurs, we have not succeeded in isolating a crystalline product.

s-*Camphorylpiperidylcarbamide*, $CO<^{NC_5H_{10}}_{NH\cdot C_{10}H_{15}O}$.

Piperidine (1 mol.) diluted with benzene was added to a solution of camphorylcarbimide in the same solvent, when heat was developed, and crystals began to separate almost immediately. After 2 days the product was drained, recrystallised from dilute alcohol, and then from benzene, which deposited lustrous, transparent needles, exceeding

2 cm. in length; when freshly withdrawn from the mother liquor, these melted at 181°, but after exposure to air during 24 hours they became opaque, and melted at 186°.

0·1438 gave 0·3642 CO_2 and 0·1230 H_2O. C = 69·08; H = 9·50.
$C_{16}H_{26}O_2N_2$ requires C = 69·05; H = 9·35 per cent.

A solution containing 0·4000 gram in 25 c.c. of chloroform gave α_D 1°17′ in a 2-dcm. tube, whence $[\alpha]_D$ 40·1°. The compound is insoluble in boiling water, and sparingly soluble in boiling light petroleum, but it dissolves readily in alcohol, acetone, ethyl acetate, chloroform, and hot benzene.

s-*Camphorylbornylcarbamide*, $CO<\begin{matrix}NH\cdot C_{10}H_{17}\\ NH\cdot C_{10}H_{15}O\end{matrix}$.

Bornylamine (1 mol.) dissolved in benzene was added to camphorylcarbimide in the same solvent. Considerable development of heat occurred, but no crystals separated until light petroleum was added, precipitating minute, colourless granules. On redissolving in benzene, and adding petroleum until the liquid became turbid, lustrous, white needles separated slowly. The derivative melts and decomposes at 305°.

0·1457 gave 0·3880 CO_2 and 0·1318 H_2O. C = 72·62; H = 10·05.
$C_{21}H_{34}O_2N_2$ requires C = 72·83; H = 9·83 per cent.

A solution containing 0·2987 gram dissolved in 25 c.c. of chloroform gave α_D 41′, whence $[\alpha]_D$ = 28·6°. The carbamide is slightly soluble in boiling light petroleum, but the crystals which separate are indefinite; it dissolves readily in benzene, ethyl acetate, alcohol, and hot acetone, crystallising from the last named in aggregates of prismatic needles.

s-*Dicamphorylcarbamide*, $CO(NH\cdot C_{10}H_{15}O)_2$.

Camphorylcarbimide was suspended in water and heated in a reflux apparatus until the penetrating odour characteristic of the substance was no longer perceptible; the product was filtered, and crystallised from dilute alcohol, which deposited aggregates of lustrous needles melting at 261°.

0·1157 gave 0·2952 CO_2 and 0·0924 H_2O. C = 69·54; H = 8·87.
$C_{21}H_{32}O_3N_2$ requires C = 70·00; H = 8·88 per cent.

A solution containing 0·5020 gram dissolved in 25 c.c. of chloroform gave α_D 1°32′ in a 2-dcm. tube, whence $[\alpha]_D$ = 38·2°. It is insoluble in boiling water, and sparingly soluble in boiling light petroleum,

from which it crystallises in silky needles on cooling; acetone, ethyl acetate, alcohol, and chloroform dissolve it freely, whilst benzene dissolves it readily when hot, a felted mass of needles being deposited on cooling.

Methyl Camphorylcarbamate (*Camphorylmethylurethane*),

$$CO<^{O \cdot CH_3}_{NH \cdot C_{10}H_{15}O}.$$

Five grams of camphorylcarbimide were dissolved in 20 c.c. of pure methyl alcohol, and allowed to remain several weeks in the desiccator; as the alcohol evaporated, a transparent, gummy syrup was deposited, in which a few small needles were embedded. On dissolving this product in alcohol, and adding water until the solution became turbid, dicamphorylcarbamide was precipitated, but the filtrate yielded slender white needles of the methylurethane, which melts at 108° after recrystallisation from petroleum.

0·2040 gave 0·4779 CO_2 and 0·1566 H_2O. C = 63·89; H = 8·53.
$C_{12}H_{19}O_3N$ requires C = 64·00; H = 8·44 per cent.

A solution containing 0·2636 gram dissolved in 25 c.c. of chloroform gave α_D 55′ in a 2-dcm. tube, whence $[\alpha]_D$ 43·5°.

Ethyl Camphorylcarbamate, $CO<^{O \cdot C_2H_5}_{NH \cdot C_{10}H_{15}O}.$

The ethylurethane, prepared as in the case of the foregoing substance, separated from the dilute alcoholic filtrate in large, transparent prisms melting at 88°.

0·1714 gave 0·4102 CO_2 and 0·1413 H_2O. C = 65·27; H = 9·18.
$C_{13}H_{21}O_3N$ requires C = 65·27; H = 8·78 per cent.

A solution containing 0·5262 gram in 25 c.c. of chloroform gave α_D 1°38′ in a 2-dcm. tube, whence $[\alpha]_D$ = 38·3°. Both urethanes are readily soluble in organic media, excepting light petroleum, and display a marked tendency to remain superfused.

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XVII.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part VII. Solution-volume and Rotation of Menthol and Menthyl Tartrates.*

By Thomas Stewart Patterson and Francis Taylor, B.Sc.

In a recent paper (this vol., p. 33) we have described the preparation of *l*-menthyl *d*-tartrate and its diacetyl derivative, and have given an account of the optical behaviour of these substances as well as of menthol. It seemed worth while to examine them in solution also in order to ascertain whether a relationship between solution-volume and rotation similar to that which has been shown to exist in the case of ethyl tartrate (Patterson, Trans., 1901, **79**, 191, 484 ; 1902, **81**, 1107 ; 1904, **85**, 1153) could be traced. The present communication records the results obtained for ethyl alcohol, benzene, and nitrobenzene.

Two or three solutions were made up in each case and their rotations and densities determined at several temperatures.

The influence of temperature-change on the rotation of the dissolved substance is given directly by the experimental figures, which are collected at the end of the paper, whilst by interpolation : (1) the molecular rotation at 20°, (2) the molecular-solution-volume at 20° of the dissolved substance for each concentration examined may be deduced, and from these in turn (3) an approximate value of the molecular rotation at 20° at infinite dilution, and (4) an analogous value for the molecular-solution-volume may be obtained.

These interpolated data are reproduced below, the constants for the respective homogeneous substances being given in the tables, so that the influence of concentration-change may be examined in each case.

The figures for the percentage composition of the solutions have been rounded off in the text.

Menthol.—The molecular rotation of fused menthol, which has a value of about $-77{\cdot}22°$ at 20°, increases slightly with rise of temperature to reach a maximum of $-77{\cdot}94°$ at 58·5°, and then diminishes again to $-77{\cdot}24°$ at 100°.

Menthol in Ethyl Alcohol.

p.	$[M]_D^{20°}$.	Volume $^{20°}$.
0·0	$-77{\cdot}70°$	172·3 c.c.
1·6	77·69	172·3 ,,
8·3	77·69	172·6 ,,
100·0	77·22	173·26 ,,

Solution in alcohol has little effect on the rotation of menthol, but a slight increase is produced. In agreement with this, there is only a small change in volume; a contraction of 0·96 c.c. corresponds with an increase of 0·48° in molecular rotation.

The figures on p. 130 show that in both the solutions examined there is, with rise of temperature from 10° to 50°, a slight but distinct increase of rotation amounting to about 0·3°. The behaviour is therefore in this respect similar to that of the homogeneous substance.

Menthol in Benzene.

p.	$[M]_D^{20°}$.	Volume $^{20°}$.
0·0	−70·4°	179·84 c.c.
1·46	70·6	179·8 ,,
7·50	71·8	178·0 ,,
100·0	77·22	173·26 ,,

From these data, it appears that whilst the rotation of solutions of menthol in benzene diminishes with increasing dilution, the volume of the dissolved substance increases. The behaviour is thus the opposite in both respects to that found for alcoholic solutions. A diminution in rotation of 6·82° corresponds with an increase of volume of 6·58 c.c.

In both solutions examined, the rotation is practically insensitive to temperature-change.

Menthol in Nitrobenzene.

p.	$[M]_D^{20°}$.	Volume $^{20°}$.
0·0	−73·60°	176·5 c.c.
1·5	73·60	176·5 ,,
2·1	73·40	176·0 ,,
6·7	73·35	175·7 ,,
30·5	73·70	174·6 ,,
100·0	77·22	173·26 ,,

Nitrobenzene as a solvent has, like benzene, the general effect of lowering the rotation of menthol. The depression, however, is not directly proportional to the concentration, since a minimum rotation of −73·28° apparently occurs about $p = 10$. Further dilution below this concentration brings about a slight increase in rotation to the value −73·6° at infinite dilution. The total change in rotation in passing from the homogeneous substance to infinite dilution is thus 3·62° and is accompanied, again as in benzene, by an increase in volume of 3·24 c.c.

Whereas, however, the rotations of alcoholic solutions increase with rise of temperature and those of benzene solutions are constant, the rotations of nitrobenzene solutions diminish fairly rapidly, a behaviour which is thus opposed also to that of fused menthol.

So far, therefore, as volume-change and rotation-change due to solution are concerned, the behaviour of menthol in these three solvents is consistent and tends strongly to support the suggestion that the two phenomena are closely related to each other. In the following table, the values of these changes are contrasted.

Rotation- and Volume-change of Menthol.

Solvent.	Total rotation-change due to solution.	Total volume-change due to solution.
Ethyl alcohol	+0·48°	−0·96 c.c.
Nitrobenzene	−3·62	+3·24 ,,
Benzene	−6·82	+6·58 ,,

A *contraction* of 0·96 c.c. in the menthol molecule on solution in alcohol produces an *increase* of rotation of 0·48°; an *expansion* of 3·24 c.c. on solution in nitrobenzene is accompanied by a *diminution* in rotation of 3·62°, whilst the greater expansion of 6·58 c.c. in benzene is accompanied by the greater diminution in rotation of 6·82°, a relationship which is almost linear.

l-*Menthyl* d-*Tartrate*.—The molecular rotation of the homogeneous compound varies fairly rapidly with temperature, having the values −288° at 0°, −284° at 20°, and −264·5° at 100°.

l-*Menthyl* d-*Tartrate in Ethyl Alcohol.*

p.	$[M]_D^{20°}$.	Volume 20°.
0·0	−306·7°	395·0 c.c.
1·22	306·2	395·8 ,,
6·7	306·1	397·7 ,,
7·9	304·2	398·3 ,,
100·0	284·0	402·0 ,, *

The relationship between rotation- and solution-volume is in this instance of a similar character to that observed for menthol in alcohol, but the changes are considerably greater. The rotation increases by 22·7°, whilst the volume diminishes by 7 c.c. The influence of temperature-change on the substance in solution is much the same as on the homogeneous ester.

l-*Menthyl* d-*Tartrate in Benzene.*

p.	$[M]_D^{20°}$.	Volume 20°.
0·0	−296·5°	407·0 c.c.
1·64	296·1	406·6 ,,
7·42	292·7	409·5 ,,
100·0	284·0	402·0 ,, *

* As this substance is very viscid, its density could not be determined directly at low temperatures, and had therefore to be found by extrapolation through nearly 100°. The value for the molecular volume is therefore liable to some error.

Benzene as a solvent brings about an increase in the rotation of menthyl tartrate, but this increase is accompanied by a slight expansion of the molecule, instead of a contraction as might be expected from the preceding results. The increase of rotation amounts to 12·5° and the expansion to about 5 c.c., but this last number, owing to there being a considerable discrepancy between the two experimental values for molecular-solution-volume (406·6 and 409·5 c.c.), is somewhat uncertain.

The rotation of the ester diminishes with rise of temperature in this solvent also, which is the same as for the homogeneous compound.

l-*Menthyl* d-*Tartrate in Nitrobenzene.*

p.	$[M]_D^{20°}$.	Volume 20°.
0·0	−245·0°	408·8 c.c.
1·42	245·3	408·8 ,,
6·49	246·3	408·2 ,,
100·0	284·0	402·0 ,, *

Solution in nitrobenzene causes a considerable diminution, 39°, in the rotation of menthyl tartrate, whilst at the same time an expansion of about 6·8 c.c. takes place in the molecule.

It is noticeable also that whilst in alcohol and benzene the rotation of menthyl tartrate diminishes with rise of temperature, it increases in nitrobenzene. In a solution of $p = 6·9$, this increase amounts to about 3° between 10° and 60°.

Comparing now these rotation- and volume-changes, the following table is obtained :

Rotation- and Volume-change of l-*Menthyl* d-*Tartrate.*

Solvent.	Total rotation-change due to solution.	Total volume-change due to solution.
Ethyl alcohol	+22·7°	−7·0 c.c.
Benzene.........	+12·5	+5·0 ,,
Nitrobenzene	−39·0	+6·8 ,,

The numbers for alcohol and nitrobenzene, it will be seen, are consistent; a contraction of 7 c.c. in the former solvent is attended by an increase in rotation of 22·7°, whilst in the latter an expansion of 6·8 c.c. accompanies a diminution of 39° in rotation. Benzene, however, although in both respects intermediate between the other two solvents, is not in close agreement. Judging by the rotation-change, a contraction of between 3 and 4 c.c. would have been expected instead of the expansion actually found.

l-*Menthyl Diacetyl*-d-*tartrate.*—The rotation of the homogeneous

* See note on page 124.

ester diminishes fairly rapidly on heating. It has the value −268·7° at 0°, −256·5° at 20°, and −227·5° at 100°.

l-Menthyl Diacetyl-d-tartrate in Ethyl Alcohol.

p.	$[M]_D^{20°}$.	Volume 20°.
0·0	−268·5°	478·0 c.c.
1·8	268·8	478·7 ,,
7·3	267·7	480·0 ,,
100·0	256·5	486·6 ,, *

Solution in alcohol thus causes an increase of 12° in the rotation of menthyl diacetyltartrate, whilst at the same time a contraction of 8·6 c.c. occurs in the molecule.

The rotation diminishes fairly rapidly with rise of temperature.

l-Menthyl Diacetyl-d-tartrate in Benzene.

p.	$[M]_D^{20°}$.	Volume 20°.
0·0	−286·5°	481·6 c.c.
1·5	286·0	481·8 ,,
7·8	284·2	482·5 ,,
100·0	256·5	486·6 ,, *

A considerable increase in rotation, 30°, takes place in this case also. Corresponding with it, however, there is only a small volume-change of 5 c.c.

The rotation diminishes with rise of temperature, much as in the fused ester.

l-Menthyl Diacetyl-d-tartrate in Nitrobenzene.

p.	$[M]_D^{20°}$.	Volume 20°.
0·0	−239·0°	483·5 c.c.
1·53	238·5	484·0 ,,
6·27	237·8	483·0 ,,
100·0	256·5	486·6 ,, *

Nitrobenzene as a solvent, unlike benzene and alcohol, causes a considerable diminution, of 17·5°, in the rotation of menthyl diacetyltartrate. There is, however, only a very slight volume change, and the above numbers are scarcely sufficient to enable one to decide definitely whether this change is an expansion or contraction. On the one hand, the value for the molecular volume, 486·6 c.c., is somewhat uncertain, whilst on the other, since the value found for the volume in 1·53 per cent. solution is greater than that in 6·27 per cent. solution,

* This value is also somewhat uncertain, because the density used in its calculation was obtained by extrapolation through a considerable range of temperature.

the value at infinite dilution may perhaps be greater than 483·5 c.c. It is, therefore, only certain that the volume-change is very small.

The rotation in this case also diminishes on heating, much as in the homogeneous ester. It may be noticed, too, that a concentration of minimum rotation possibly exists at about $p = 10$.

On comparing the values of the rotation- and volume-changes for menthyl diacetyltartrate, we obtain the following table :

Rotation- and Volume-change of l-*Menthyl Diacetyl*-d-*tartrate.*

Solvent.	Total rotation change due to solution.	Total volume change due to solution.
Alcohol	+12·0°	−8·6 c.c.
Benzene	+30·0	−5·0 ,,
Nitrobenzene.........	−17·5	−3·1 ,,

In this instance, whilst the rotation changes are fairly large, the volume-changes are small, and the relationship between the variables is not so satisfactory as in the other two cases. Thus, although the molecular contraction in benzene is less than in alcohol, the rotational change is greater, and although the diminution in rotation due to solution in nitrobenzene ought, judging by analogy, to be accompanied by an expansion of the molecule, very little change, and that apparently a contraction, occurs, but, as has already been mentioned, the volume-change in the last case is rather uncertain.

We consider that, on the whole, these results help to confirm the suggestion that rotation in solution and molecular-solution-volume are closely related phenomena. For menthol, the facts are in complete agreement with theory. With menthyl tartrate, the results for alcohol and nitrobenzene are in close agreement, although the relationship between the two variables in benzene is anomalous. Difficulties are met with for menthyl diacetyltartrate also, but here, as has been pointed out, although in alcohol and benzene the relationship is not a quantitative one, it is in agreement with theory, in so far as, in both cases, contraction brings about increased rotation. Thus, out of the nine examples studied, contraction produces increased rotation in four instances, expansion causes diminished rotation in three instances, contraction accompanies diminished rotation in one case, whilst expansion accompanies increased rotation in another. Thus, out of nine observations, seven are in accord with the theory, and of the two exceptions one at least is somewhat doubtful.

Attention may be directed to two further points illustrated by the data obtained in this investigation. In the table below, numbers are given showing the sensitiveness of the rotations of the active compounds examined, to change of volume.

Substance.	Total variation of rotation.	Total variation of volume.	Molecular volume.	Variation of rotation due to 1 per cent. volume-change.
Menthol	7·3°	7·54 c.c.	173·3 c.c.	1·7°
l-Menthyl *d*-tartrate	61·7	13·8 ,,	402·0 ,,	18·0
l-Menthyl diacetyl-*d*-tartrate	47·5	5·5 ,,	486·6 ,,	42·0

An example will show how these numbers are obtained. Solution in alcohol increases the rotation of menthyl tartrate by 22·7°, whilst benzene diminishes the rotation by 39°. The total range is therefore 61·7°. Similarly, the total range of volume is 13·8 c.c., the molecular volume being 402 c.c. A contraction of 1 per cent., that is, of 4·02 c.c., occasions a rotation change of 18°. From the last column in the table, it will be seen that the sensitiveness increases greatly with increase in the size of the molecule. The larger the molecule, the greater is the effect produced on its rotation by a given percentage volume change.

In conclusion, the following table gives a survey of the rotation values obtained:

	$[M]_D^{20°}$.			
		At infinite dilution in		
	Homogeneous.	Alcohol.	Benzene.	Nitrobenzene
Menthol	−77·22°	−77·7°	−70·4°	−73·6°
l-Menthyl *d*-tartrate	284·0	306·7	296·5	245·0
l-Menthyl diacetyl-*d*-tartrate	256·5	268·5	286·5	239·0

The numbers show that the relationship amongst the rotation values for a given set of related active compounds is not constant, even when all are subjected to what one might expect to be similar conditions. Thus, the ratio of the above numbers for alcohol is different from that for the homogeneous condition, whilst both in turn differ from the ratios obtained in benzene and nitrobenzene.

It is thus clear that any comparison of rotation data which have been determined in different solvents is apt to be very misleading, and that even data determined under the same conditions, as in the present investigation, have only a special, and but little general, value. The results hitherto obtained, however, seem to indicate that for any given active substance it may be possible to obtain an expression connecting the rotation in solution with that in the homogeneous condition by taking the volume-change into account.

Thus we have for menthol, from some of the results described in this paper (p. 124), the expression:

$$[M]_D^{20°}(\text{soln.}) = [M]_D^{20°}(\text{homog.}) + 0{\cdot}97°\, dv,$$

where dv is the change of volume for a particular solvent and 0·97° * is the average increase in rotation for unit alteration in volume. From this formula, we obtain the following numbers :

Solvent.	dv.	$[M]_D^{20°}$ solution Calculated.	Found.
Alcohol	−0·96 c.c.	−78·1°	−77·7°
Benzene	+6·58 ,,	70·8	70·4
Nitrobenzene	+3·24 ,,	74·1	73·6

The calculated and experimental values are thus in fair agreement, and, although expressions giving equally good results cannot be established for the other compounds examined, we hope that future investigation will result in the explanation of existing anomalies and the discovery of further regularities.

Experimental Data.

Menthol in Benzene.

$p = 1·45555$. Density of benzene = 0·878918 at 20°/4°.

t.	$a_D^{t°}$ (400 mm.).	Density.	$[a]_D^{t°}$.	$[M]_D^{t°}$.
9·1°	−2·343°	0·8914	−45·15°	−70·43°
17·0	2·301	0·8819	44·83	69·93
23·0	2·323	0·8755	45·57	71·09
32·6	2·287	0·8653	45·39	70·81

Densities Determined:

Temperature	17·96°	20°	25·07°	30·5°
Density	0·88092	0·878752 *	0·87336	0·8676

* The values marked thus have been obtained by interpolation from the other data given.

$p = 7·49708$.

t.	$a_D^{t°}$ (400 mm.).	Density.	$[a]_D^{t°}$.	$[M]_D^{t°}$.
7·1°	−12·339°	0·8916	−46·15°	−71·99°
17·6	12·124	0·8811	45·89	71·59
28·0	11·931	0·8709	45·69	71·28
34·2	11·926	0·8646	45·99	71·73

Densities Determined:

Temperature	17·45°	20°	25·7°	32·05°
Density	0·88130	0·878719 *	0·87295	0·86632

* This value is obtained by dividing the total range of rotation (7·3°) by the total change of volume (7·54 c.c.).

Menthol in Ethyl Alcohol.

$p = 1·5749$. Density of alcohol = 0·790801 at 20°/4°.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
12·0°	−2·500°	0·7992	−49·66°	−77·47°
19·0	2·490	0·7932	49·83	77·74
27·9	2·470	0·7856	49·91	77·86

Densities Determined:

Temperature	18·15°	20°	23·87°	29·06°
Density	0·79397	0·792386 *	0·78908	0·78460

$p = 8·26794$.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
12·0°	−13·243°	0·8058	−49·69°	−77·51°
17·6	13·167	0·8011	49·70	77·53
18·1	13·173	0·8006	49·78	77·66
29·7	13·065	0·7909	49·95	77·92
41·6	12·985	0·7807	50·29	78·46
46·9	12·888	0·7762	50·21	78·33

Densities Determined:

Temperature ...	18·32°	20°	23·71°	29·47°	35·17°
Density	0·80049	0·799072 *	0·79595	0·79104	0·78617

Menthol in Nitrobenzene.

$p = 1·4539$. Density of nitrobenzene = 1·20353 at 20°/4°.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
22·5°	−3·272°	1·1947	−47·09°	−73·46°
32·9	3·223	1·1839	46·80	73·00

Densities Determined:

Temperature	19·25°	20°	28·93°	43·2°
Density	1·19796	1·19723 *	1·1885	1·1745

$p = 2·05718$.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
8·5°	−4·728°	1·2063	−47·63°	−74·30°
24·0	4·595	1·1909	46·89	73·14
39·0	4·472	1·1760	46·21	72·08

Densities Determined:

Temperature	19·6°	20°	31·7°	41·7°
Density	1·19152	1·19474 *	1·18324	1·17352

$p = 6·6542$.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
9·8°	−14·950°	1·1855	−47·37°	−73·89°
25·3	14·532	1·1706	46·63	72·74
46·4	14·180	1·1503	46·29	72·21
67·2	13·790	1·1301	45·84	71·51
78·7	13·607	1·1198	45·65	71·22

Densities Determined:

Temperature	17·05°	20°	24·42°	47·15°
Density	1·17858	1·17573 *	1·17142	1·1495

$p = 30·4894$.

t.	$\alpha_D^{t°}$ (100 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
19·1°	−15·715°	1·0892	−47·30°	−73·78°
22·7	15·60	1·0859	47·10	73·47
25·3	15·52	1·0834	46·98	73·28
29·7	15·42	1·0795	46·84	73·06

Densities Determined:

Temperature	19·6°	20°	31·6°	41·2°	54·1°
Density............	1·0888	1·08848 *	1·0777	1·0690	1·0571

---

l-*Menthyl* d-*Tartrate in Ethyl Alcohol.*

$p = 1·2119$. Density of alcohol = 0·790801 at 20°/4°.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
12·0°	−2·835°	0·8001	−73·10°	−311·4°
22·5	2·741	0·7911	71·48	304·5

Densities Determined:

Temperature	17·74°	20°	26·33°
Density	0·795300	0·793348 *	0·787913

$p = 6·69547$.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
12·8°	−15·730°	0·8110	−72·42°	−308·5°
14·9	15·682	0·8094	72·34	308·2
25·5	15·285	0·8002	71·34	303·9
28·1	15·210	0·7980	71·18	303·2
34·1	15·030	0·7927	70·80	301·6
36·4	14·962	0·7907	70·65	301·0
62·7	14·150	0·7679	68·80	293·1

Densities Determined:

Temperature	17·64°	20°	26·46°	42·24°
Density	0·806938	0·804914 *	0·799372	0·785674

$p = 7·92984$. Density of alcohol = 0·792198 at 20°/4°.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
9·7°	−18·743°	0·8176	−72·26°	−307·8°
19·1	18·367	0·8098	71·50	304·5
26·0	18·097	0·8037	70·98	302·3
33·9	17·77	0·7969	70·30	299·5

Densities Determined:

Temperature	19·75°	20°	30·38°	41·6°
Density	0·80904	0·808828 *	0·79992	0·79008

l-*Menthyl* d-*Tartrate in Benzene.*

$p = 1·63747$. Density of benzene = 0·87869 at 20°/4°.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
10·5°	−4·085°	0·8910	−70·00°	−298·2°
14·0	4·055	0·8873	69·79	297·3
16·1	4·039	0·8850	69·71	297·0
27·5	3·952	0·8733	69·10	294·4
29·0	3·938	0·8715	69·01	294·0

Densities Determined:

Temperature	19·82°	20°	27·7°	39·75°
Density	0·88121	0·881017 *	0·87285	0·86004

$p = 7·41659$.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
9·4°	−18·552°	0·8992	−69·53°	−296·2°
17·3	18·227	0·8915	68·92	293·6
25·8	17·858	0·8828	68·17	290·4
33·3	17·637	0·8753	67·90	289·2
37·2	17·425	0·8713	67·41	287·2

Densities Determined:

Temperature	18·1°	20°	26·05°	30·4°
Density	0·89087	0·88893 *	0·88242	0·87831

l-*Menthyl* d-*Tartrate in Nitrobenzene.*

$p = 1·42535$. Density of nitrobenzene = 1·20353 at 20°/4°.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
16·7°	−3·945°	1·2040	−57·46°	−244·8°
28·4	3·932	1·1927	57·82	246·3
36·2	3·923	1·1850	58·05	247·3

Densities Determined:

Temperature	18·51°	20°	27·6°	43·3°
Density	1·20234	1·20088 *	1·19345	1·17809

$p = 6·48726$.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
10·1°	−17·970°	1·2014	−57·65°	−245·6°
18·4	17·905	1·1935	57·81	246·2
21·1	17·875	1·1908	57·84	246·4
51·9	17·567	1·1609	58·28	248·3
56·9	17·532	1·1560	58·41	248·8

Densities Determined:

Temperature	19·3°	20°	30·25°	50·25°
Density	1·19236	1·19168 *	1·18176	1·16248

---

l-*Menthyl Diacetyl*-d-*tartrate in Ethyl Alcohol.*

$p = 1·7888$. Density of alcohol = 0·790801 at 20°/4°.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
18·7°	−3·007°	0·7955	−52·83°	−269·4°
21·6	2·983	0·7930	52·57	268·1
29·6	2·920	0·7862	51·91	264·7
41·3	2·840	0·7759	51·16	260·9

Densities Determined:

Temperature	17·72°	20°	24·78°	40·66°
Density	0·79642	0·794465 *	0·79037	0·77647

$p = 7·26494$.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
13·0°	−12·487°	0·8117	−52·94°	−270·0°
17·4	12·369	0·8080	52·68	268·7
23·9	12·175	0·8024	52·22	266·3
40·2	11·684	0·7883	51·01	260·1

Densities Determined:

Temperature	16·63°	20°	30·69°
Density	0·808676	0·805775 *	0·796572

l-*Menthyl Diacetyl*-d-*tartrate in Benzene.*

$p = 1{\cdot}49569$. Density of benzene = 0 878822 at 20°/4°.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
7·5°	−3·148°	0·8947	−58·80°	−299·9°
16·0	3·013	0·8854	56·87	290·0
26·0	2·875	0·8747	54·94	280·2
41·2	2·687	0·8582	52·31	266·8

Densities Determined:

Temperature	22·6°	20°	33·46°	40·8°
Density	0·87827	0 881057 *	0·86676	0·8588

$p = 7{\cdot}80199$.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
8·0°	−16·385°	0·9032	−58·12°	−296·4°
17·9	15·640	0·8930	56·10	286·1
35·0	14 522	0·8749	53·20	271·3

Densities Determined:

Temperature	20°	20·23°	29·05°	43°
Density	0·8·0537 *	0·890276	0·881188	0·86651

l-*Menthyl Diacetyl*-d-*tartrate in Nitrobenzene.*

$p = 1{\cdot}52859$. Density of nitrobenzene = 1·20353 at 20°/4°.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
9·9°	−3·487°	1 2106	−47·12°	−240·3°
17·0	3·447	1 2038	46·85	238·9
27·5	3 390	1·1935	46·46	236·9
49·9	3·270	1·1721	45·62	232·6

Densities Determined:

Temperature	19·28°	20°	30·45°	39·2°
Density	1·20163	1·20092 *	1·19074	1·18202

$p = 6{\cdot}26591$.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
17·0°	−14·000°	1·1960	−46·69°	−238·1°
32·7	13·733	1·1809	46·39	236·6
44·7	13·490	1·1693	46·02	234·7
61·0	13·140	1·1535	45·44	231·7

Densities Determined:

Temperature	20°	20·5°	32·12°	45·77°
Density	1·19307 *	1·19259	1·18134	1·16815

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XVIII.—*A Further Analogy between the Asymmetric Nitrogen and Carbon Atoms.*

By HUMPHREY OWEN JONES.

THE phenomena brought to light by the recent investigations on the stereoisomerism of quinquevalent nitrogen compounds are remarkable and perplexing on account of their apparently contradictory nature. The existence of isomerism in compounds of the type Na.b.c.d,X, hitherto established definitely by Wedekind for one compound only, the non-existence of isomerides of the type Na_2b.c.X, and the existence of isomerides of the type Na_3b.X, observed by Kipping only when the radicles b and X both contain an asymmetric carbon atom, and even then only in certain cases, are facts which are extremely difficult to reconcile with one another, and have rendered necessary new assumptions as to the structure and the mode of formation of these compounds (compare Kipping, Trans., 1903, **83**, 937, 1149; Jones, Trans., 1903, **83**, 1404, and B.A. Report, 1904).

In these circumstances, any further definite information as to the behaviour of these compounds, and particularly as to the similarity or difference between their behaviour and that of compounds containing an asymmetric carbon atom, is of importance.

The analogy between asymmetric carbon and nitrogen compounds, so far as optical activity is concerned, has now been established for a number of compounds which contain the phenyl, benzyl, and methyl groups with a variable fourth radicle; thus, the allyl compound has been resolved (Pope and Peachey, Trans., 1899, **75**, 1127), also the ethyl (Jones, Trans., 1904, **85**, 223), the *iso*propyl and *iso*amyl (Thomas and Jones, *Proc. Camb. Phil. Soc.*, 1904, **13**, 33), and the propyl compound (Wedekind, private communication).

It was therefore considered of interest to try to establish a further analogy between the asymmetric carbon and nitrogen atoms as regards their behaviour during the synthesis of asymmetric compounds. It was to be expected, if the analogy was valid in this case, that, when a tertiary amine in which one of the groups contained an asymmetric carbon atom combined with an alkyl iodide so as to make the nitrogen

atom asymmetric, unequal quantities of the two possible isomerides would be produced, which, not being enantiomorphously related, might be separated by ordinary processes. If the tertiary amine were inactive, then four compounds should be formed, which would be enantiomorphously related in pairs, and would probably combine to form two externally compensated inactive compounds separable by ordinary means.

The two compounds which could be produced from an active amine might be conventionally represented by plane projections of the space formulæ, thus:

```
  a b c                     a b c
   \|/                       \|/
    C                         C
    |          and            |          ,
R'—N—R''                  R''—N—R'
   / \                       / \
 R'''  X                    X   R'''
```

and would bear to one another a relation similar to that of the α- and β-glucoheptonic acids or the two $\alpha\beta$-dihydroxybutyric acids.

This expectation has been realised, and it has been definitely established that two compounds are produced when an active tertiary amine combines with an alkyl iodide to form an asymmetric nitrogen compound so that the analogy with carbon is valid. The two compounds produced are called respectively α- and β-compounds, the α-compound being that which has a rotation of the same sign as the amine. There is possibly some risk of confusion arising, since Wedekind has called the two phenylbenzylmethylallylammonium compounds α- and β-, but it was thought that the following considerations justified the course adopted; the risk of confusion is small, α- and β- best indicate the nature of the isomerism in question, and the analogy between this case and that of the addition of hydrocyanic acid to the sugars is very close.

Extending the analogy between carbon and nitrogen atoms still further, it was to be expected that when two asymmetric nitrogen atoms are simultaneously produced, four compounds would be formed which would combine in pairs, or, if the two nitrogen atoms were the same, then three compounds should be produced, as in the case of tartaric acid. This case has been examined by Wedekind (*Ber.*, 1903, **36**, 1165, 3796), the compound used being ethyl ethylene-bistetrahydro*iso*quinolinium-2-acetate iodide, but the compounds, if formed, could not be separated.

The amine used was methyl-*l*-amylaniline, which was dextrorotatory ($[\alpha]_D = 11\cdot06°$). This was combined with methyl, allyl, and benzyl iodides.

The compound with methyl iodide is practically inactive, thus showing that the effect of the carbon atom is very small, and supporting the conclusion that nitrogen compounds of the type $Na_2b.c.X$ cannot be optically active.

The compounds with allyl and benzyl iodides are dextrorotatory, the strength of the rotation depends on the conditions of formation, changes on recrystallisation, and in chloroform solution the rotation changes and finally becomes constant, corresponding to a state of equilibrium between the isomerides.

In the case of the allyl compound, the less soluble compound can be isolated by crystallisation. In the case of the benzyl compound, separation cannot be effected in this way, as there is only a slight difference of solubility and, what is still more important, the two compounds are easily transformed one into the other by dissociation into tertiary amine and benzyl iodide followed by recombination.

The separation has been effected by means of the camphorsulphonates, which are more stable and show greater differences in properties.

The following observations on the benzyl compounds show conclusively that two compounds are produced which are not enantiomorphously related to one another.

(1) The rotatory power of the salt depends on the solvent in which it is produced.

(2) The *l*-camphorsulphonate of the α-base and the *d*-camphorsulphonate of the β-base differ in their melting point, crystalline form, and rotatory powers, and are therefore not enantiomorphously related.

(3) The α- and β-iodides have different melting points and solubilities (in alcohol).

(4) Solutions of the α-iodide (dextrorotatory) and the β-iodide (lævorotatory) in chloroform undergo a rapid change in rotatory power, until finally both have the same slight dextrorotation, $[\alpha]_D = 2{\cdot}8°$. This corresponds to a change of one isomeride into the other by dissociation into benzyl iodide and tertiary amine (compare auto-racemisation of active compounds, Trans., 1901, **79**, 828; 1904, **85**, 229), until equilibrium is set up with a definite ratio between the concentrations of the α- and β-compounds. These facts can be accounted for only by supposing that two compounds exist which are not optical antimers. The formation of two such compounds can be explained on either of the two views already expressed by Kipping and the author as to the mode of formation of these quinquevalent compounds.

A preliminary note on this work was published in May last (*Proc. Camb. Phil. Soc.*, 1904, **12**, 466); since that time a paper by Scholtz appeared (*Ber.*, 1904, **37**, 3627), in which similar results obtained with coninium derivatives are described. In the four cases examined, it has been shown that, when the nitrogen atom in *d*-coniine is made

asymmetric, two different compounds were produced which were separated by fractional crystallisation.

The general relations between the α- and β-compounds (the α-compound is the one with the lower melting point) are similar to those herein described, but with this important distinction, to which Scholtz has drawn attention, that the α- and β-coninium derivatives are more stable and cannot be transformed into one another; even although three of the compounds contain the benzyl group they appear to remain unchanged in chloroform solution.

l-*Amyl bromide* was prepared by the action of 270 grams of phosphorus tribromide on 264 grams of *l*-amyl alcohol ($[\alpha]_D^{15^\circ} - 5{\cdot}6^\circ$).

The phosphorus bromide was dropped slowly into the alcohol, the mixture allowed to stand, then warmed, and afterwards washed repeatedly, first with water, then dilute sodium carbonate solution, and finally several times with concentrated sulphuric acid to remove amyl alcohol. The bromide is a colourless liquid boiling at 120—120·5°/760 mm.; α_D in a 1-dcm. tube at 15° was + 4·56° and $d_{15}^{4} =$ 1·224, hence $[\alpha]_D + 3{\cdot}8^\circ$. Le Bel (*Bull. Soc. chim.*, 1876, **25**, 505) gives the boiling point as 117—119°, $d = 1{\cdot}225$, and α_D in 1-dcm. tube at 15° = 4·24°.

Methyl-l-*amylaniline*.—Methylaniline and *l*-amyl bromide were respectively mixed in the proportion of two molecules to one, and heated for about six hours on a water-bath; on standing, a mass of long, prismatic crystals separated out. These were filtered off, and after recrystallising from ethyl acetate were found to melt at 97—98° and to be methylaniline hydrobromide.

The oil was fractionated, in some cases under reduced pressure and in others under the ordinary pressure with a dephlegmator. It was found that the fractionation under the ordinary pressure effected a complete separation of the base more rapidly than fractionation under reduced pressure; the oil was finally distilled once under reduced pressure.

The tertiary amine is a colourless oil boiling at 131—132° under 16 mm. and at 244—245° under 764 mm. pressure.

0·1097 gave 0·3260 CO_2 and 0·1125 H_2O. C = 81·0; H = 11·4.
0·2120 ,, 0·6325 CO_2 ,, 0·2110 H_2O. C = 81·36; H = 11·0.
0·1550 ,, 11·2 c.c. nitrogen * at 15° and 744 mm. N = 8·25.
$C_{12}H_{19}N$ (177) requires C = 81·35; H = 10·7; N = 7·95 per cent.

The density of the amine was found to be 0·9220 at 15° as a mean of several concordant determinations made on different preparations; α_D in a 1-dcm. tube at 15° was found to be + 10·2° in the same way, hence

* The caustic potash solution over which the nitrogen was collected contained one part of KOH in two parts of water.

$[\alpha]_D^{15°} = 11·06°$ and $[M]_D = 19·8°$. The refractive index at 15° was determined for sodium light, and for the red and blue lines (α and γ) of the hydrogen spectrum.

Light.	Refractive index.	Molecular refractive power, $\frac{\mu^2 - 1}{\mu^2 + 2} \frac{M}{d}$.	Calculated from atomic refractive powers.
Na	1·5313	59·4	—
Red H	1·5462	60·8	59·02
Blue H	1·5268	59·0	57·59

An attempt was made to prepare salts of this amine and, if possible, to confirm the above constants with the amine recovered from the pure salt. Unfortunately, none of the salts examined was found to be suitable for this purpose. The hydrochloride can be obtained crystalline and melts at 138°, but does not recrystallise well from any of the ordinary solvents. The tartrates and the camphorates decompose when recrystallised, as also does the platinichloride. The *d*- and *l*-camphorsulphonates and the *d*-bromocamphorsulphonate were not obtained in a crystalline state.

The rotatory power of a solution of the amine in a slight excess of hydrochloric acid was determined and it was found that $[\alpha]_D = 14·8°$, hence $[M]_D = 26·3°$. A solution of the amine with the calculated quantity of *d*-camphorsulphonic acid and a trace of hydrochloric acid was found to give $[\alpha]_D$ (for the *d*-camphorsulphonate) = 22·2°.

Hence $[M]_D = 90·4°$ and $[M]_D$ for the basic ion = 38·7°.

This result suggests the conclusion that in the formation of the camphorsulphonate a larger quantity of one of the two possible compounds is formed than of the other.

Combination of the Tertiary Amine with Alkyl Iodides.

Phenyldimethyl-l-*amylammonium Iodide.*—A mixture of the tertiary amine and methyl iodide in molecular quantities deposited a gummy mass which became partly crystalline on standing, or in some cases deposited crystals in the first instance. Combination took place to the extent of about 30 per cent. in seven days. The solid was dissolved in alcohol, in which it is very soluble, and allowed to stand; large, colourless crystals were deposited which melted sharply at 146—147° without apparent decomposition. A solution containing 1·748 grams in 25 c.c. alcohol gave a rotation of not more than 0·01° in a 2-dcm. tube.

The effect of the asymmetric carbon atom seems to be almost negligible in this salt, and the nitrogen appears to have no rotatory power. This supports the conclusion previously arrived at (Trans.,

1903, **83**, 1420), that compounds of the type $Na_2b.c.X$ do not exist in optically active forms. Scholtz (*loc. cit.*) found that only one dibenzylconinium iodide was produced.

*Phenylmethylallyl-*l*-amylammonium Iodides.*

A mixture of the tertiary amine and allyl iodide in molecular proportions soon sets to a mass of crystals held together by a little gummy matter; the crystals melt at 123—129°. A similar mixture *plus* a little alcohol deposited no solid on standing; on the addition of ether, a crystalline precipitate was produced which melted at 134—136°. A determination of the rotatory power of the crude salt in alcoholic solution gave the following result:

0·901 gram in 25 c.c. gave α_D + 0·12° in a 2-dcm. tube; $[\alpha]_D = 1·66°$.

On examination under a microscope, the salt is seen to be a mixture of two different kinds of crystals, one being long, thin prisms often aggregated into sheaves, the other very small, thick prisms which are more soluble in alcohol than the longer prisms. The salt deposited from alcoholic solution consists chiefly of the long prisms and the melting point rises on recrystallisation until it becomes constant at 156—157°; the dextrorotatory power increases at the same time. This is therefore the α-salt.

The determinations of the rotatory power were made both in alcohol and in chloroform, but chiefly the latter, in which the salt is much more soluble and the rotatory power is also much greater.

A determination of the rotatory power in alcohol gave the following result:

0·859 gram in 25 c.c. gave $\alpha_D = 0·98°$ in a 2-dcm. tube, hence $[\alpha]_D = 14·3°$. The specific rotatory power of the recrystallised salt in chloroform is about 21·8° and gradually falls very slowly until it reaches a constant value of 3·1°.

The following example is typical:

0·861 grams in 25 c.c. gave $\alpha_D = 1·5°$ in a 2-dcm. tube.

After 24 hours, $\alpha_D = 1·31°$. After 120 hours, $\alpha_D = 0·45°$.

„ 72 „ $\alpha_D = 0·84°$. „ ∞ „ $\alpha_D = 0·22°$.

$[\alpha]_D = 21·78°$ (initial); $[\alpha] = 3·1°$ (final).

The change of rotatory power which takes place in this case is very probably due to the change of one of the two possible compounds (α) into the other (β) until equilibrium is attained, the change taking place by dissociation into the tertiary amine and allyl iodide and subsequent recombination, just as in the auto-racemisation of the active

compounds observed by Pope and Harvey (Trans., 1901, **79**, 830) and by the writer (Trans., 1904, **85**, 229). In these cases, the salt split into amine and benzyl iodide and the change took place much more rapidly. The velocity of the transformation in this case is roughly about one-fifth that of the active phenylbenzylmethylallylammonium iodide as determined by the author, and about one-thirtieth that of the corresponding benzyl compound to be described later.

0·2715 gave 0·5175 CO_2 and 0·1702 H_2O. C = 51·9; H = 6·96.
$C_{15}H_{24}NI$ requires C = 52·1; H = 6·95 per cent.

The more soluble β-compound could not be isolated in a pure state as it is rather soluble in alcohol and tends to become coloured owing to the accumulation of small amounts of decomposition products.

However, a solution of 0·5 gram in 25 c.c. alcohol, decolorised as far as possible by means of sulphur dioxide, was found to be lævorotatory to the extent of about 0·1° in a 2-dcm. tube, so that $[\alpha]_D = -2·5°$.

Phenylbenzylmethyl-l-*amylammonium Iodides.*

A mixture of the amine and benzyl iodide in molecular proportions sets very rapidly to a crystalline mass. It was found that a better result was obtained by adding some solvent, when good crystals of the iodide were deposited.

Various solvents were used, and the rotatory power of the iodide deposited from mixtures of equal concentration in the same time was found to vary. The results of the numerous experiments made are summarised below; the rotatory power of the crude salt was taken in solution in chloroform.

In each case, 2·18 grams of benzyl iodide and 1·77 grams of amine were made up to 6 c.c. with solvent.

Solvent.	Melting point of salt.	$[\alpha]_D$.
Alcohol	113—115°	4·0
Ether	118—121	3·5
Ethyl acetate	118—121	3·9
Chloroform.........	114—117	12·9

It was found that in all cases the rotatory power of the salt deposited depended very much on the quantity which had been deposited. The following selected results for alcohol serve to illustrate this effect.

Weight of salt formed......	2·0	1·0	0·8	0·5 grams
$[\alpha]_D$..........................	4·0°	6·3°	7·0°	8·9°

These results account for the phenomena observed in a magnetic field (*Proc. Camb. Phil. Soc., loc. cit.*, 468). In these experiments, the determination of the quantity of the deposit was at first overlooked; in the same magnet, it diminished with increasing strength of the field chiefly on account of a small rise in temperature; when different magnets were used, and the temperature carefully regulated, the difference in $[\alpha]_D$ of the salt was traced to the difference in the quantity of salt formed. With magnetic fields up to 20,000 units, there appears to be no effect on the relative quantities of the two compounds produced.

On recrystallisation of this iodide from warm or hot alcohol, the melting point gradually rises to 141—142°, while the rotatory power alters but little.

In alcohol, 0·149 gram in 10·048 grams solution gave $\alpha_D = 0 \cdot 12°$ in a 2-dcm. tube; $p = 1 \cdot 48$, $d = 0 \cdot 810$, hence $[\alpha]_D = 5 \cdot 0°$.

In chloroform, 0·387 gram in 21·103 grams solution gave $\alpha_D = 0 \cdot 35°$ in a 2-dcm. tube; $p = 1 \cdot 84$, $d = 1 \cdot 48$, hence $[\alpha]_D = 6 \cdot 45°$.

0·334 gram in 16·562 grams solution gave $\alpha_D' = 0 \cdot 38$ in a 2-dcm. tube; $p = 2 \cdot 02$, $d = 1 \cdot 48$, hence $[\alpha]_D = 6 \cdot 42°$.

The rotation of all the solutions in chloroform fell rapidly until a constant rotation was reached of $[\alpha]_D + 2 \cdot 8°$. It is clearly not possible to separate the α- and β-isomerides in this way; the difficulty arises from the small difference in the solubility of the two compounds, and the ease with which they undergo mutual transformation in solution.

There is a greater difference between the two corresponding camphorsulphonates, and these were therefore prepared and purified.

Unfortunately, neither the *d*- nor *l*-camphorsulphonates corresponding to both α- and β-iodides could be prepared and purified, but the *d*-camphorsulphonate of the β-compound and the *l*-camphorsulphonate of the α-compound could be isolated by fractional crystallisation.

The iodide purified as already described was converted into the camphorsulphonate in the usual way by boiling a mixture of the iodide and silver *d*- or *l*-camphorsulphonate with acetone or ethyl acetate.

*β-Phenylbenzylmethyl-*l*-amylammonium* d*-Camphorsulphonate.*

The *d*-camphorsulphonate was recrystallised repeatedly from acetone until its melting point became constant. The rotatory power gradually fell until eventually the aqueous solution was found to be very slightly lævorotatory; a 4·5 per cent. solution had α_D in 2-dcm. tube $= -0 \cdot 02°$. Hence the basic ion appears to have $[M]_D = -52°$ approximately.

The *d*-camphorsulphonate crystallises in long, white prisms, which, on heating, begin to turn blue at 130° and melt to a blue liquid at 150—152°.

Analysis indicates that the salt crystallises with a molecule of acetone of crystallisation.

0·1470 gave 0·3718 CO_2 and 0·1096 H_2O. C = 68·8; H = 8·30.
0·1966 „ 0·4961 CO_2 „ 0·1510 H_2O. C = 68·8; H = 8·55.
$C_{29}H_{41}NSO_4,C_3H_6O$ requires C = 68·9; H = 8·44 per cent.
$C_{29}H_{41}N \cdot SO_4$ requires C = 69·7; H = 8·24 per cent.

*β-Phenylbenzylmethyl-*l*-amylammonium iodide* was precipitated from the aqueous solution of the *d*-camphorsulphonate by the addition of potassium iodide solution.

The crude iodide melts at 130—131°, and after crystallising from cold alcohol, at 131—132°, it therefore melts at a lower temperature than the mixture. The rotatory power was determined in alcohol and in chloroform.

In alcohol, 0·169 gram in 9·240 grams of solution gave $\alpha_D = -0·47°$ in a 2-dcm. tube; $p = 1·831$, $d = 0·814$, hence $[\alpha]_D = -15·8°$.

In chloroform, 0·217 gram in 17·696 grams of solution gave $\alpha_D = -0·68°$ in a 2-dcm. tube; $p = 1·22$, $d = 1·480$, hence $[\alpha]_D = -18·8°$.

The rotatory power of this solution fell off rapidly; after 4 hours, $\alpha_D = -0·18°$, and after 48 hours $\alpha_D = +0·10°$, corresponding to $[\alpha]_D = +2·78°$, a value identical with the final value obtained for the chloroform solutions of the iodide purified by recrystallisation from alcohol.

The solubility of this iodide in alcohol at 15° was found to be 2·1 grams in 100 grams of alcohol.

Heating in alcoholic solution caused the rotatory power to fall off, and the iodide deposited eventually gave $[\alpha]_D$ about 7° in chloroform solution.

Both the chloroform solution and the hot alcoholic solutions smell strongly of benzyl iodide, so that the change which occurs in both cases must be due to dissociation into the tertiary amine and benzyl iodide, with subsequent combination to form both α- and β-compounds, and, as previously stated, this change takes place much more rapidly than the racemisation of the two active compounds, which also contain the benzyl radicle.

Analysis of the β-iodide gave the following result:

0·1435 gave 0·3030 CO_2 and 0·0871 H_2O. C = 57·56; H = 6·72.
$C_{19}H_{26}NI$ requires C = 57·7; H = 6·58 per cent.

*α-Phenylbenzylmethyl-*l*-amylammonium* l*-camphorsulphonate* was prepared from the iodide recovered from the more soluble part of the *d*-camphorsulphonate, and which had $[\alpha]_D$ in chloroform = 12°, and was recrystallised several times from a mixture of acetone and light petroleum, and then finally from ethyl acetate or acetone alone until the melting point became constant. This salt differs in appearance

and properties from the *d*-camphorsulphonate described above; it crystallises in feathery prisms melting sharply at 161—161·5°.

The salt, which is at first lævorotatory, becomes eventually strongly dextrorotatory.

0·182 gram in 12·157 gram of solution gave $\alpha_D = +1·48°$ in a 2 dcm. tube; hence $p = 1·5$, $d = 1·002$, $[\alpha]_D = 49·4°$, and $[M]_D = 247°$.

The value of $[M]_D$ for the basic ion is therefore about 299°. This high value agrees with that obtained for the corresponding *iso*amyl compound (*Proc. Camb. Phil. Soc.*, 1904, **13**, 35).

Analysis of this salt gave the following numbers:

0·1358 gave 0·3456 CO_2 and 0·1015 H_2O. C = 69 6; H = 8·32.
$C_{29}H_{41}N{\cdot}SO_4$ requires C = 69·7; H = 8·24 per cent.

a-Phenylbenzylmethyl-l-*amylammonium iodide* was precipitated from the aqueous solution of the *l*-camphorsulphonate by the addition of potassium iodide solution. The crude iodide melted at 132°, and after crystallising from cold alcohol several times it melted at 144—145° and therefore at a higher temperature than the β-compound or the mixture. Rotatory power determinations were made in alcohol and in chloroform; the following are typical examples.

In alcohol, 0·150 gram in 12·400 grams of solution gave $\alpha_D = 1·16°$; hence $p = 1·21$, $d = 0·815$, $[\alpha]_D = 59·0°$.

In chloroform, 0·136 gram in 15·737 grams of solution gave $\alpha_D = 1·65°$ in a 2-dcm. tube, $p = 0·864$, $d = 1·475$; hence $[\alpha]_D = 65°$. After 1 hour, $\alpha_D = 1·30°$; 48 hours, $\alpha_D = 0·07°$, corresponding to $[\alpha]_D = 2·75°$.

The solubility of the α-iodide in alcohol at 15° is 1·48 grams in 100 grams of alcohol.

It is clear therefore that in the formation of an asymmetric nitrogen atom in a compound containing an asymmetric carbon atom two compounds are formed. These compounds differ in properties such as melting point and solubility and in rotatory power, and are readily transformed one into the other until equilibrium is attained in chloroform solution, when one of the radicles is either allyl or benzyl. The compounds, when sufficiently stable, can be separated by crystallisation.

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XIX.—*Nitrogen Halogen Derivatives of the Sulphonamides.*

By Frederick Daniel Chattaway.

The study of nitrogen halogen derivatives, that is, of compounds containing halogen directly attached to nitrogen, has yielded many valuable scientific results. Perhaps the most notable members of this class of substances are the bromoamides, which, on heating with caustic alkalis yield primary amines, and the acylphenyl-chloro- and -bromoamides, which, under the influence of hydrogen chloride or bromide, undergo an intramolecular rearrangement whereby the halogen enters into the phenyl nucleus. Both these classes of derivatives, however, so readily undergo isomeric change that they are not well adapted for a study of the behaviour of halogen when attached to nitrogen.

It seemed possible that a number of syntheses which have failed when tried with somewhat unstable nitrogen halogen derivatives might succeed if attempted with stable compounds not liable readily to undergo isomeric change. Such substances are found in the nitrogen halogen derivatives of the sulphonamides, and the present paper contains a description of a number of these compounds, the various reactions of which are being further investigated.

The sulphonamides are distinguished by the great readiness with which they form well-crystallised derivatives in which all the aminic hydrogen is replaced by halogen when acted upon by hypochlorous acid at the ordinary temperature, for example :

$$C_6H_5{\cdot}SO_2{\cdot}NH{\cdot}CH_3 + HOCl \rightleftarrows C_6H_5{\cdot}SO_2{\cdot}NH(CH_3){<}^{OH}_{Cl} \rightleftarrows C_6H_5{\cdot}SO_2{\cdot}N(CH_3)Cl + H_2O.$$

The sulphonchloroamides so produced exhibit great stability when compared with other chloroamides, for example, the reverse change only takes place very slowly even on boiling with a large excess of water. Those containing two chlorine atoms attached to the nitrogen melt without decomposition and can frequently be heated considerably above their melting points without undergoing any change ; they explode when heated by a direct flame, the tetrachloroamides derived from the disulphonamides resembling nitrogen chloride itself in the violence with which they detonate. When similarly heated, the sulphonalkylchloroamides do not detonate, but decompose rapidly with the evolution of gas.

They all readily take part in those characteristic reactions which distinguish the nitrogen halogen from the carbon halogen linking, the halogen being in every case replaced by hydrogen and the sulphon-

amide regenerated; for example, they liberate chlorine when heated with hydrochloric acid, iodine chloride or iodine when treated with an equivalent quantity or an excess of hydriodic acid, and set free sulphur when treated with hydrogen sulphide; when heated with alcohol, they form ethyl hypochlorite, which at once breaks down into aldehyde and hydrogen chloride,

$$C_6H_5\cdot SO_2\cdot NCl_2 + 2C_2H_5\cdot OH = C_6H_5\cdot SO_2\cdot NH_2 + 2C_2H_5\cdot OCl,$$

and with hydrogen cyanide they form cyanogen chloride.

The sulphondichloroamides dissolve readily in warm aqueous solutions of the alkaline hydroxides, forming salts of the sulphonmonochloroamides, which separate as the liquids cool in large crystals containing water of crystallisation, for example:

$$C_6H_5\cdot SO_2\cdot NCl_2 + 2KOH = C_6H_5\cdot SO_2K\colon NCl + KOCl + H_2O.$$

These salts are very easily soluble in water and are comparatively stable in aqueous or alkaline solution; they are, however, slowly hydrolysed when boiled for some hours with aqueous alkalis, the original sulphonamide being regenerated. The water of crystallisation is lost when the crystals are heated to 100° or when they are kept in a vacuum over phosphoric oxide. The anhydrous salts are very stable; when heated, they do not melt, but explode at temperatures varying with the nature of the substance, and to some extent with the rapidity with which they are heated.

There is every reason to believe that in the salts of the bromoamides the metal is not attached to nitrogen * but to oxygen, and that they are in reality salts of the bromo*iso*amides. Although it has not been directly proved, there are similar reasons for believing that the salts obtained from the sulphondichloroamides are derivatives of the sulphon*iso*chloroamides, $RSO(OH)\colon NCl$, and have a constitution represented by the general formula $RSO(OM)\colon NCl$.

On acidifying aqueous solutions of these salts one would expect to obtain the sulphon*iso*chloroamides or the sulphonmonochloroamides produced from them by intramolecular rearrangement; such compounds, however, have not yet been obtained. On adding acetic acid to such solutions, white, crystalline solids are precipitated, which, on recrystallisation, prove to be the sulphondichloroamides, whilst equivalent quantities of the sulphonamides remain in solution. This is probably due to a progressive hydrolysis of the sulphon*iso*chloroamides first formed, and the production, by the agency of the hypochlorous acid so formed, of the much more sparingly soluble sulphondichloroamides:

$$RSO(OH)\colon NCl + H_2O = RSO_2\cdot NH_2 + HOCl.$$

$$RSO(OH)\colon NCl + HOCl = RSO(OH)\colon NCl_2\cdot OH = RSO_2\cdot NCl_2 + H_2O.$$

* Hantzsch and Dollfuss, *Ber.*, 1902, **35**, 249.

All the aromatic sulphonamides easily yield very stable substituted nitrogen bromides, which show the typical behaviour of this type of compound, as they do not readily undergo isomeric change. A few sulphondibromoamides have been studied by Hoogewerff and van Dorp (*Rec. Trav. Chim.*, 1887, 6, 373), and were described in their researches upon the action of potassium hypobromite on amides: among others, benzenesulphondibromoamide and benzene-*m*-disulphontetrabromoamide. These chemists, however, did not prepare them by a very convenient method or one capable of giving a good yield.

The method of preparing substituted nitrogen bromides by means of hypobromous acid, which has been applied with success in many other cases, is similarly successful here. All the sulphonamides and alkyl sulphonamides readily react with this reagent, which replaces all the aminic hydrogen by bromine, and a number of typical derivatives of the aromatic sulphonamides have been prepared in this way. For example:

$$C_6H_5{\cdot}SO_2{\cdot}NH{\cdot}CH_3 + HOBr \rightleftharpoons C_6H_5{\cdot}SO_2{\cdot}NH(CH_3)\Big<{}^{Br}_{OH} \rightleftharpoons C_6H_5{\cdot}SO_2{\cdot}N(CH_3)Br + H_2O.$$

The yields are theoretical.

The sulphondibromoamides resemble the sulphondichloroamides; they crystallise well and behave similarly on heating. They are, however, bright yellow in colour. Although they are unusually stable as compared with nitrogen bromides generally, they slowly decompose on keeping, bromine being liberated. They interact with hydrochloric acid, hydriodic acid, hydrogen sulphide, and alcohol in the manner characteristic of nitrogen bromides, the sulphonamide in each case being regenerated.

Although hydrolysed when heated with water or with somewhat dilute acetic acid, they are remarkable among nitrogen bromides for the slowness with which these actions take place.

As has been noted by Hoogewerff and van Dorp (*loc. cit.*) in the case of the compounds which they prepared, the sulphondibromoamides interact readily with a solution of sodium or potassium hydroxide, salts of the sulphonmonobromoamides being produced. These salts are pale yellow, stable substances which readily dissolve in water and crystallise beautifully with varying amounts of water of crystallisation, the latter being lost when the salts are exposed over phosphoric oxide under reduced pressure. The anhydrous salts do not melt, but decompose explosively when strongly heated. It is probable that they are similar in constitution to the analogous salts derived from the sulphondichloroamides, and that they are derivatives of the unknown sulphon*iso*bromoamides, $R{\cdot}SO(OH){:}NBr$. The latter compounds are not obtained on acidifying solutions of these salts, sulphondibromoamides and sulphon-

amides being produced in equivalent amount, probably in the manner suggested to explain the similar behaviour of the chloro-compounds.

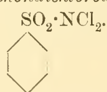
When solutions of these salts in caustic alkalis are heated, they readily undergo hydrolysis; the yellow colour of the solution disappears as the action proceeds, and a solution of the sulphonamide in the caustic alkali together with alkaline bromide and bromate are formed.

The sulphonalkylbromoamides, $RSO_2{\cdot}NR'Br$, are prepared by the same method with equal ease. They are pale yellow, well-crystallised compounds which, in virtue of the halogen attached to the nitrogen, resemble other nitrogen bromides in chemical behaviour. They are comparatively stable substances, which, however, decompose with reddening and evolution of gas on heating above their melting points. As with the corresponding chlorine derivatives, those containing the benzyl group are the least stable, and decompose slowly even when kept in a dry atmosphere screened from light. Various reactions of these compounds are being investigated.

I. *Sulphondichloroamides and Sulphonalkylchloroamides.*

Benzenesulphondichloroamide,

$SO_2{\cdot}NCl_2$.



This substance was first mentioned by Kastle (*Amer. Chem. J.*, 1895, **17**, 704), who suggested its use instead of chlorine water as a reagent for bromine and iodine; it was subsequently briefly described by Kastle, Keiser, and Bradley (*Amer. Chem. J.*, 1896, **18**, 491). They obtained it by leading chlorine into a solution of benzenesulphonamide in caustic potash, heating the solid which separated with hot water, and subsequently dissolving the residue in alcohol and precipitating the dichloroamide by water as pearly-white laminæ which melted at 70°. These methods of preparation and purification are, however, not the most suitable.

Benzenesulphondichloroamide and all other sulphondichloroamides are most conveniently prepared by adding the corresponding sulphonamide to an excess of a saturated solution of bleaching powder, in which they all readily dissolve, and then slowly pouring acetic acid into the cooled solution. The sulphondichloroamides at once separate as oily liquids which solidify quickly to white, crystalline solids. These may be filtered off, and are practically pure dichloroamides. As, however, these solids are not easily and conveniently dried, it is best to add to the acid liquid sufficient chloroform to dissolve them completely. It is advisable to shake the chloroform solution with a further small

quantity of fresh acidified bleaching powder solution to ensure the absence of any trace of unchanged sulphonamide. The chloroform solution is then separated, dried over fused calcium chloride, and the solvent driven off on the water-bath in a current of air, taking care that the temperature of the evaporating liquid does not rise much above 20°. The dichloroamides are then left as beautifully crystalline white solids, which may be recrystallised from chloroform, or, better, by dissolving them in warm chloroform and adding a little warm petroleum, when, on cooling, they separate in colourless crystals with a scarcely perceptible yellow tint.

Benzenesulphondichloroamide is easily soluble in chloroform or in acetic acid, and crystallises from these solvents in transparent, colourless plates with a very faint yellow tint. It is sparingly soluble in petroleum and water. It is hydrolysed on prolonged boiling with water or somewhat diluted acetic acid; the action is, however, very slow, and from such partly hydrolysed solutions the dichloroamide still remaining separates on cooling in a nearly pure state, as its solubility in these solvents is less than that of benzenesulphonamide. It melts at 76°, and when heated above this point remains for some time unchanged, but decomposes with ebullition at about 200°, giving off chlorine, nitrogen, hydrogen chloride, and benzenesulphonic chloride. When heated rapidly in a flame, it decomposes with a feeble explosion. This and the other chloroamides described in the paper were analysed by dissolving them in acetic acid, adding excess of potassium iodide, and titrating the liberated iodine with a standard solution of sodium thiosulphate.

0·3905 liberated I = 69·2 c.c. $N/10$ I. Cl as NCl = 31·41.
$C_6H_5O_2NCl_2S$ requires Cl as NCl = 31·37 per cent.

When benzenesulphondichloroamide is added to a somewhat dilute cold solution of caustic potash or soda, it dissolves forming a pale yellow liquid from which, on the addition of a saturated solution of the alkali hydroxide, salts of benzenesulphonmonochloroamide containing water of crystallisation slowly separate in long, colourless, flattened prisms. These are still more readily obtained by cautiously dissolving the sulphondichloroamide in a warm 10 per cent. solution of sodium or potassium hydroxide; on slowly cooling the pale yellow liquid, the salts crystallise out well in glittering, transparent, colourless, flattened prisms. If, after the dichloroamide has dissolved, the solution is heated nearly to boiling, a very vigorous reaction accompanied by violent ebullition sets in, and if much of the dichloroamide has been used the salt may separate out in small crystals even while the solution is hot. This behaviour seems to indicate that the alkali hydroxide first combines with the sulphondichloroamide, the salt of

the sulphon*iso*chloroamide being formed from this additive product by a splitting off of alkaline hypochlorite, some of the heat being derived from the rapid transformation of the latter into chloride and chlorate.

Identical salts are precipitated on passing chlorine in limited amount into solutions of the sulphonamides in excess of strong caustic alkalis, but this method of preparation is not a convenient one. These salts, which are probably derivatives of benzenesulphon*iso*chloroamide, $C_6H_5\cdot SO(OH)\colon NCl$, are very stable in presence of alkalis, and considerable heating is needed to effect complete hydrolysis, which, however, takes place with the formation of the original sulphonamide and alkaline chloride and chlorate when a solution in aqueous alkali is heated for some hours at 100°. No transformation of these salts has hitherto been observed to take place under these conditions. They are very easily soluble in water, although with some slight hydrolysis, and are again precipitated from solution on adding strong alkali. Similar results are obtained by warming the sulphondichloroamides with a solution of calcium or barium hydroxide.

Potassium benzenesulphonchloroamide, $C_6H_5\cdot SO_2K\colon NCl,H_2O$.

This salt was prepared as above described by dissolving benzenesulphondichloroamide in an excess of a warm 10 per cent. solution of potassium hydroxide. On cooling, the pale yellow solution deposited the salt in long, colourless, transparent prisms; these were filtered off, rapidly washed with a little cold water, pressed between filter paper, and dried for a short time in the air. A quantity of this salt was analysed by dissolving it in a solution of potassium iodide, acidifying with acetic acid, and titrating the liberated iodine with sodium thiosulphate.

0·4185 liberated I = 34·2 c.c. *N*/10 I. Cl as NCl = 14·48.

A further quantity was exposed in a vacuum over phosphoric oxide for four days until its weight became constant.

0·4349 lost 0·0310 H_2O. H_2O = 7·13 per cent.

A quantity similarly dried was analysed as before.

0·2937 liberated I = 25·5 c.c. *N*/10 I. Cl as NCl = 15·39.

$C_6H_5O_2NClSK,H_2O$ requires Cl as NCl = 14·31. H_2O = 7·27.

$C_6H_5O_2NClSK$ requires Cl as NCl = 15·43 per cent.

The salt is very soluble in water, giving a pale yellow solution; it is less soluble in a strong solution of potassium hydroxide, and crystallises easily from this in colourless, transparent, glittering, long prisms, apparently six-sided with domed ends.

When heated rapidly, the dry salt does not melt, but explodes some

what violently with decomposition and liberation of a black solid, probably carbon, at about 140—145°. The temperature of decomposition depends, however to some extent on the rapidity with which the salt is heated

Sodium benzenesulphonchloroamide, $C_6H_5 \cdot SO_2Na\colon NCl,3H_2O$.

This compound was prepared exactly as the potassium salt, than which it is somewhat more sparingly soluble in water; it crystallises in long, colourless, transparent, flattened prisms with domed ends. It is very easily soluble in water giving a pale yellow solution, less easily in a solution of sodium hydroxide,

0·2632 liberated I = 19·7 c.c. *N*/10 I. Cl as NCl = 13·27 per cent.

When dried for several days over phosphoric oxide until no further loss in weight occurred, the crystals did not fall to powder, but became opaque, retaining, to a certain extent, their crystalline shape.

0·2052 liberated I = 19·1 c.c. *N*/10 I. Cl as NCl = 16·49.
$C_6H_5O_2NClSNa,3H_2O$ requires Cl as NCl = 13·25.
$C_6H_5O_2NClSNa$ requires Cl as NCl = 16·59 per cent.

When heated rapidly, the anhydrous salt does not melt, but explodes with violence at about 180—185°.

Toluene-o-sulphondichloroamide,

$SO_2 \cdot NCl_2$ / CH_3 (benzene ring structure).

Toluene-*o*-sulphonamide was powdered and dissolved in an excess of a cooled solution of bleaching powder. On adding acetic acid slowly, the dichloroamide separated as an oil which did not solidify even on strongly cooling. It was therefore extracted by chloroform, the solution in chloroform again shaken with acidified bleaching powder, and afterwards removed, dried, and the solvent evaporated off in a current of air on a water-bath. A pale yellow, oily liquid was left which slowly solidified to a beautifully crystalline, colourless mass. It is very soluble in chloroform and freely soluble in petroleum. It crystallises from light petroleum in clusters of slender, colourless plates which melt at 33°.

0·2694 liberated I = 44·9 c.c. *N*/10 I. Cl as NCl = 29·54
$C_7H_7O_2NCl_2S$ requires Cl as NCl = 29·53 per cent.

*Potassium toluene-*o*-sulphonchloroamide*, $CH_3 \cdot C_6H_4 \cdot SO_2K \colon NCl, H_2O$.

This salt was prepared as previously described, using a 10 per cent. solution of potassium hydroxide; it crystallises in glittering, transparent, colourless prisms.

0·3688 liberated 28·1 c.c. *N*/10 I. Cl as NCl = 13·50.
$C_7H_7O_2NClSK,H_2O$ requires Cl as NCl = 13·54 per cent.

The hydrated salt loses its water of crystallisation when kept for some days in a vacuum over phosphoric oxide, but alters very little in appearance.

0·2590 liberated I = 21·1 c.c. *N*/10 I. Cl as NCl = 14·44.
$C_7H_7O_2NClSK$ requires Cl as NCl = 14·54 per cent.

The anhydrous salt explodes feebly when heated to about 145°.

*Sodium toluene-*o*-sulphonchloroamide*, $CH_3 \cdot C_6H_4 \cdot SO_2Na \colon NCl, 2H_2O$.

This salt crystallises in long, colourless, transparent, somewhat flattened prisms.

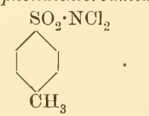
0·2130 liberated I = 16·5 c.c. *N*/10 I. Cl as NCl = 13·73.
$C_7H_7O_2NClSNa,2H_2O$ requires Cl as NCl = 13·44 per cent.

When dried over phosphoric oxide in a vacuum or heated on a water-bath, the crystals lose their water of crystallisation and become opaque.

0·2005 liberated I = 17·7 c.c. N/10 I. Cl as NCl = 15·65.
$C_7H_7O_2NClSNa$ requires Cl as NCl = 15·57 per cent.

The anhydrous salt does not melt, but explodes with some violence when heated to about 170—175°.

*Toluene-*p*-sulphondichloroamide*,



This was first obtained by Kastle, Keiser, and Bradley (*loc. cit.*), but no analysis was published; they give its melting point as 80°, and state that it crystallises in smaller crystals than the benzene derivatives and is rather more difficult to obtain pure and dry.

It is easily prepared by the general method described above. It is moderately soluble in chloroform, sparingly so in petroleum; and

crystallises from chloroform mixed with a little petroleum, in very long, colourless, flattened, four-sided prisms terminated by short pyramids (m. p. 83°).

0·2190 liberated I = 36·5 c.c. *N*/10 I. Cl as NCl = 29·54.
$C_7H_7O_2NCl_2S$ requires Cl as NCl = 29·53 per cent.

Potassium toluene-p-*sulphonchloroamide*, $CH_3{\cdot}C_6H_4{\cdot}SO_2K{:}NCl,H_2O$.

This salt, prepared from a 10 per cent. solution of potassium hydroxide, crystallises in large, colourless, four-sided plates, often elongated into long, flattened prisms. The salt dried in air gave the following numbers on analysis:

0·3564 liberated I = 27·2 c.c. *N*/10 I. Cl as NCl = 13·53 per cent.

A quantity was kept for some days over phosphoric oxide in a vacuum until its weight was constant; the crystals became opaque.

0·4839 lost 0·0335. H_2O = 6·92 per cent.

A further quantity similarly dried was analysed:

0·3043 liberated I = 24·8 c.c. *N*/10 I. Cl as NCl = 14·44.
$C_7H_7O_2NClSK,H_2O$ requires Cl as NCl = 13·54. H_2O = 6·88.
$C_7H_7O_2NClSK$ requires Cl as NCl = 14·54 per cent.

When heated rapidly, the anhydrous salt does not melt, but explodes with violence at about 160—165°.

Sodium toluene-p-*sulphonchloroamide*, $CH_3{\cdot}C_6H_4{\cdot}SO_2Na{:}NCl,3H_2O$.

This salt crystallises in long, flattened, colourless, transparent prisms.

0·4806 liberated I = 34·3 c.c. Cl as NCl = 12·65.
$C_7H_7O_2NClSNa,3H_2O$ requires Cl as NCl = 12·58 per cent.

When exposed over phosphoric oxide in a vacuum for some days, or when heated on a water-bath for a short time, the salt loses its water of crystallisation; the crystals become opaque, but retain roughly their original shape.

0·3082 liberated I = 27·1 c.c. Cl as NCl = 15·59.
$C_7H_7O_2NClSNa$ requires Cl as NCl = 15·57 per cent.

The anhydrous salt explodes with violence when heated to about 175—180°.

Nitrobenzene-m-*sulphondichloroamide*,

$SO_2\cdot NCl_2$ (benzene ring with NO_2 in the meta position)

This compound crystallises from chloroform, in which it is moderately soluble, in colourless, glittering, six-sided plates with a faint yellow tint (m. p. 121°).

0·2952 liberated I = 43·7 c.c. *N*/10 I. Cl as NCl = 26·24.
$C_6H_4O_4N_2Cl_2S$ requires Cl as NCl = 26·15 per cent.

Potassium nitrobenzene-m-*sulphonchloroamide*,
$NO_2\cdot C_6H_4\cdot SO_2K{:}NCl,x(H_2O)$,
crystallises from a strongly alkaline solution in very small, pale yellow, transparent plates, which, on drying over phosphoric oxide in a vacuum, lose water of crystallisation and become opaque. The water of crystallisation was not estimated, as, owing to the smallness of the crystals, it was found difficult to remove all adhering water. The anhydrous salt was analysed:

0·2056 liberated I = 14·7 c.c. *N*/10 I. Cl as NCl = 12·67.
$C_6H_4O_4N_2ClSK$ requires Cl as NCl = 12·9 per cent.

The anhydrous salt explodes with incandescence and deposition of carbon at about 155°. Although the dry salt can be heated on a water-bath for a short time without decomposition, if its solution in caustic potash is heated, it darkens in colour, heat is evolved, and a violent action occurs, resulting in the formation of a purple solution from which acids precipitate tarry substances the nature of which has not yet been determined. All the salts of the two sulphonchloroamides containing a NO_2 group which have been investigated behave in this manner.

Sodium nitrobenzene-m-*sulphonchloroamide*,
$NO_2\cdot C_6H_4\cdot SO_2Na{:}NCl,x(H_2O)$,
crystallises in small, very pale yellow plates. These, like those of the potassium salt, were too small to be satisfactorily dried by pressing between paper in order to determine the water of crystallisation. When dried over phosphoric oxide in a vacuum, they lose their water of crystallisation and become opaque, forming a nearly white, crystalline powder.

0·2772 liberated I = 21·3 c.c. *N*/10 I. Cl as NCl = 13·62.
$C_6H_4O_4N_2ClSNa$ requires Cl as NCl = 13·7 per cent.

When heated rapidly, the dry salt explodes with incandescence and deposition of carbon at about 175°.

2-*Nitrotoluene*-p-*sulphondichloroamide*,

$$C_6H_3(CH_3)(NO_2)\cdot SO_2\cdot NCl_2$$

This compound crystallises from chloroform, in which it is moderately soluble, in very pale yellow, transparent, four-sided prisms (m. p. 101°).

0·3082 liberated I = 43·5 c.c. *N*/10 I. Cl as NCl = 25·02.
$C_7H_6O_4N_2Cl_2S$ requires Cl as NCl = 24·87 per cent.

Potassium 2-*nitrotoluene*-p-*sulphonchloroamide*,

$$C_6H_3Me(NO_2)\cdot SO_2K\colon NCl,x(H_2O),$$

crystallises in small, pale yellow, transparent plates, which lose water of crystallisation and become opaque when dried in a vacuum over phosphoric oxide.

0·2121 liberated I = 14·4 c.c. *N*/10 I. Cl as NCl = 12·03.
$C_7H_6O_4N_2SClK$ requires Cl as NCl = 12·27 per cent.

The anhydrous salt, when heated to about 160°, explodes. The sodium salt resembles this substance; both behave like the salts of nitrobenzene-*m*-sulphonchloroamide when heated with aqueous caustic alkali.

Benzene-m-*disulphontetrachloroamide*,

$$C_6H_4(SO_2\cdot NCl_2)_2$$

This compound is easily soluble in chloroform; it crystallises from a mixture of this solvent and light petroleum in colourless, transparent rhombs (m. p. 128°).

0·1694 liberated I = 36·1 c.c. *N*/10 I. Cl as NCl = 37·77.
$C_6H_4O_4N_2Cl_4S_2$ requires Cl as NCl = 37·91 per cent.

When strongly heated, the melted substance explodes with a violence recalling the explosion of nitrogen chloride itself, carbon being deposited. It readily dissolves in a warm solution of potassium or sodium hydroxide, forming salts of benzene-*m*-disulphondichloroamide, which, however, are so soluble that they have not been satisfactorily isolated.

Naphthalene-1-sulphondichloroamide,

$SO_2{\cdot}NCl_2$

This compound crystallises from a mixture of chloroform and petroleum in large, transparent plates of a pale yellow colour ; this colour, which is more marked than is usual in nitrogen chlorides derived from colourless amides, appears to be the real colour of the compound and not to be due to impurity ; its solution in chloroform is also much deeper yellow than that of other similar compounds ; it melts at 91°.

0·3280 liberated I = 47·4 c.c. *N*/10 I. Cl as NCl = 25·61.
$C_{10}H_7O_2NCl_2S$ requires Cl as NCl = 25·68 per cent.

Potassium and *sodium naphthalene-1-sulphonchloroamides* crystallise out in small, colourless plates when a solution of the dichloroamide in warm caustic potash or soda is allowed to cool. When dried over phosphoric oxide, their composition is represented by the formulæ $C_{10}H_7{\cdot}SO_2K{:}NCl$ and $C_{10}H_7{\cdot}SO_2Na{:}NCl$.

Naphthalene-2-sulphondichloroamide,

$SO_2{\cdot}NCl_2$,

is somewhat difficult to obtain crystalline as it is very soluble in all solvents ; it slowly crystallises from light petroleum containing a very little chloroform in thick, colourless, transparent plates (m. p. 68°).

0·3514 liberated I = 50·2 c.c. *N*/10 I. Cl as NCl = 25·32.
$C_{10}H_7O_2NCl_2S$ requires Cl as NCl = 25·68 per cent.

Potassium naphthalene-2-sulphonchloroamide, $C_{10}H_7{\cdot}SO_2K{:}NCl,3H_2O$, which is comparatively sparingly soluble, crystallises in large, very thin, transparent, pearly-white plates.

0·3868 liberated I = 22·9 c.c. *N*/10 I. Cl as NCl = 10·49.
$C_{10}H_7O_2NClSK,3H_2O$ requires Cl as NCl = 10·62 per cent.

When dried for some days over phosphoric oxide in a vacuum, the crystals give up their water of crystallisation and lose their transparency.

0·1873 of the anhydrous salt liberated I = 13·2 c.c. *N*/10 I. Cl as NCl = 12·49.
$C_{10}H_7O_2NClSK$ requires Cl as NCl = 12·67 per cent.

When heated, the dry salt explodes feebly at about 170° with deposition of carbon.

Sodium naphthalene-2-sulphonchloroamide, $C_{10}H_7\cdot SO_2Na\colon NCl,H_2O$, is also sparingly soluble; it crystallises from a solution of sodium hydroxide in large, pearly-white, thin, transparent plates.

0·2546 liberated I = 17·5 c.c. *N*/10 I. Cl as NCl = 12·18.
$C_{10}H_7O_2NClSNa,H_2O$ requires Cl as NCl = 12·58 per cent.

On standing over phosphoric oxide in a vacuum for some days, the water of crystallisation is lost, but the crystals change very little in appearance.

0·1392 of the anhydrous salt liberated I = 10·5 c.c. *N*/10 I. Cl as NCl = 13·37.
$C_{10}H_7O_2NClSNa$ requires Cl as NCl = 13·44 per cent.

The dry salt does not melt, but explodes feebly at about 180° with deposition of carbon.

Naphthalene-2 : 7-disulphontetrachloroamide,

$Cl_2N\cdot O_2S$–$C_{10}H_6$–$SO_2\cdot NCl_2$.

This compound is moderately soluble in chloroform and crystallises from this solvent in clusters of short, colourless, transparent pyramids which melt at 165°. The melted substance explodes with great violence when strongly heated.

0·2530 liberated I = 47·3 c.c. *N*/10 I. Cl as NCl = 33·14.
$C_{10}H_6O_4N_2Cl_4S_2$ requires Cl as NCl = 33·44 per cent.

The potassium and sodium salts of naphthalene-2 : 7-disulphondichloroamide crystallise in long, colourless, hair-like crystals. When dried over phosphoric oxide, their composition is represented by the formulæ $C_{10}H_6(SO_2K\colon NCl)_2$ and $C_{10}H_6(SO_2Na\colon NCl)_2$. They decompose explosively with the formation of brown, earthy-looking powders at about 145—150° and 165—170° respectively.

Anthraquinone-2-sulphondichloroamide, $C_{14}H_7O_2\cdot SO_2\cdot NCl_2$, crystallises from chloroform, in which it is moderately soluble, in clusters of bright yellow, transparent plates (m. p. 177°).

0·2554 liberated I = 28·2 c.c. *N*/10 I. Cl as NCl = 19·57.
$C_{14}H_7O_4NCl_2S$ requires Cl as NCl = 19·91 per cent.

Arylsulphonalkylchloroamides.

Compounds of this nature are produced with great readiness by the action of an aqueous solution of hypochlorous acid on the sulphonalkylamides. They are most conveniently prepared by dissolving the corresponding sulphonalkylamide in chloroform and shaking the solution for some minutes with a solution of hypochlorous acid made by adding an excess of potassium hydrogen carbonate to a *N*/10 solution of sodium hypochlorite. It is best to shake finally for a few minutes with a fresh quantity of hypochlorous acid solution, then to separate, dry the chloroform solution over fused calcium chloride, and drive off the solvent in a current of air. The sulphonalkylchloroamides are left as white, crystalline solids or as pale yellow, viscid oils, which can be made to solidify by cooling and stirring with a little light petroleum. They can be recrystallised from chloroform or petroleum, or, as a rule, better from a mixture of the two solvents. They all crystallise particularly well.

A number of compounds derived from various methyl, ethyl, propyl, and benzyl derivatives of the sulphonamides have been obtained. Those containing methyl, ethyl, and propyl groups are comparatively stable, whereas those in which benzyl occurs undergo spontaneous decomposition after a few hours, even when kept in dry air; chlorine and hydrogen chloride are liberated, while an odour resembling that of benzaldehyde becomes apparent.

When rapidly heated, they all decompose with evolution of gas, but without explosion.

Benzenesulphonmethylchloroamide, $C_6H_5 \cdot SO_2 \cdot NCl \cdot CH_3$, crystallises from a mixture of chloroform and petroleum in colourless, short rhombs (m. p. 81°).

0·4819 liberated I = 47·1 c.c. *N*/10 I. Cl as NCl = 17·32.
$C_7H_8O_2NClS$ requires Cl as NCl = 17·24 per cent.

Benzenesulphonethylchloroamide, $C_6H_5 \cdot SO_2 \cdot NCl \cdot C_2H_5$, colourless plates (m. p. 52°).

0·4248 liberated I = 39 c.c. *N*/10 I. Cl as NCl = 16·27.
$C_8H_{10}O_2NClS$ requires Cl as NCl = 16·14 per cent.

Benzenesulphonbenzylchloroamide, $C_6H_5 \cdot SO_2 \cdot NCl \cdot CH_2 \cdot C_6H_5$, colourless, slender prisms (m. p. 109°).

0·3042 liberated I = 21·5 c.c. *N*/10 I. Cl as NCl = 12·53.
$C_{13}H_{12}O_2NClS$ requires Cl as NCl = 12·59 per cent.

This substance is comparatively unstable; on keeping in a desiccator over phosphoric oxide, it slowly decomposed, giving off chlorine and

hydrogen chloride, while a strong odour resembling that of benzaldehyde was noted. In two days, the percentage of Cl as NCl fell to 11·60 per cent.

Toluene-p-*sulphonmethylchloroamide*, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NCl \cdot CH_3$, crystallises in colourless prisms which melt at 82°.

0·4530 liberated I = 41·5 c.c. *N*/10 I. Cl as NCl = 16·24.
$C_8H_{10}O_2NClS$ requires Cl as NCl = 16·14 per cent.

Toluene-p-*sulphonethylchloroamide*, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NCl \cdot C_2H_5$, crystallises in colourless, six-sided plates (m. p. 86°).

0·4862 liberated I = 41·8 c.c. *N*/10 I. Cl as NCl = 15·24.
$C_9H_{12}O_2NClS$ requires Cl as NCl = 15·17 per cent.

Toluene-p-*sulphonpropylchloroamide*, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NCl \cdot C_3H_7$, is very readily soluble in chloroform and in light petroleum; it crystallises in colourless plates (m. p. 58°).

0·5844 liberated I = 46 c.c. *N*/10 I. Cl as NCl = 13·95.
$C_{10}H_{14}O_2NClS$ requires Cl as NCl = 14·31 per cent.

Toluene-p-*sulphonbenzylamide*, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot CH_2 \cdot C_6H_5$.

This and a number of similar compounds not hitherto described have been prepared by adding the calculated quantity of the amine, either anhydrous or in aqueous solution, to the sulphonic chloride, either solid or dissolved in ether or chloroform. Vigorous action as a rule took place and much heat was generated. After standing for some hours to complete the action, the calculated quantity of potassium hydrogen carbonate dissolved in water was added, the whole being finally warmed for a time on the water-bath. The solid thus obtained was then recrystallised, except when otherwise stated, from alcohol.

Toluene-*p*-sulphonbenzylamide crystallises in colourless, transparent, six-sided prisms terminated by pyramids (m. p. 116°).

Toluene-p-*sulphonbenzylchloroamide*, $CH_3 \cdot C_6H_4 \cdot SO_2 \cdot NCl \cdot CH_2 \cdot C_6H_5$. This compound crystallises in colourless, six-sided plates (m. p. 136°).

0·3359 liberated I = 22·8 c.c. *N*/10 I. Cl as NCl = 12·03.
$C_{14}H_{14}O_2NClS$ requires Cl as NCl = 11·99 per cent.

Nitrobenzene-m-*sulphonmethylamide*, $NO_2 \cdot C_6H_4 \cdot SO_2 \cdot NH \cdot CH_3$, very pale yellow, flattened prisms (m. p. 125°).

Nitrobenzene-m-*sulphonmethylchloroamide*,

$SO_2{\cdot}NCl{\cdot}CH_3$

NO_2 ,

forms pale yellow, transparent, four-sided plates (m. p. 136°).

0·3958 liberated I = 31·6 c.c. *N*/10 I. Cl as NCl = 14·15.

$C_7H_7O_4N_2ClS$ requires Cl as NCl = 14·14 per cent.

Nitrobenzene-m-*sulphonethylamide*, $NO_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}C_2H_5$, small, colourless plates with a faint tinge of yellow (m. p. 81°).

Nitrobenzene-m-*sulphonethylchloroamide*, $NO_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NCl{\cdot}C_2H_5$, forms large, very pale yellow, four-sided plates (m. p. 84°).

0·5097 liberated I = 38·7 c.c. *N*/10 I. Cl as NCl = 13·45.

$C_8H_9O_4N_2ClS$ requires Cl as NCl = 13·39 per cent.

Nitrobenzene-m-*sulphonbenzylamide*, $NO_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot}C_6H_5$, colourless plates with a faint tinge of yellow (m. p. 101°).

Nitrobenzene-m-*sulphonbenzylchloroamide*,

$NO_2{\cdot}C_6H_4{\cdot}SO_2{\cdot}NCl{\cdot}CH_2{\cdot}C_6H_5$,

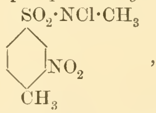
crystallises from chloroform, in which it is moderately soluble, in colourless, slender prisms with the faintest perceptible yellow tint (m. p. 142°).

0·4280 liberated I = 26·3 c.c. *N*/10 I. Cl as NCl = 10·89.

$C_{13}H_{11}O_4N_2ClS$ requires Cl as NCl = 10·85 per cent.

2-*Nitrotoluene*-p-*sulphonmethylamide*, $NO_2{\cdot}C_6H_3Me{\cdot}SO_2{\cdot}NH{\cdot}CH_3$, very pale yellow prisms (m. p. 93°).

2-*Nitrotoluene*-p-*sulphonmethylchloroamide*,



crystallises from chloroform, in which it is moderately soluble, in very pale yellow, transparent, four-sided prisms (m. p. 90°).

0·3160 liberated I = 23·8 c.c. *N*/10 I. Cl as NCl = 13·35.

$C_8H_9O_4N_2ClS$ requires Cl as NCl = 13·39 per cent.

2-*Nitrotoluene*-p-*sulphonethylamide*, $NO_2{\cdot}C_6H_3Me{\cdot}SO_2{\cdot}NH{\cdot}C_2H_5$, short, thick, very pale yellow prisms (m. p. 87°).

2-*Nitrotoluene*-p-*sulphonethylchloroamide*,

$NO_2{\cdot}C_6H_3Me{\cdot}SO_2{\cdot}NCl{\cdot}C_2H_5$,

crystallises in pale yellow, four-sided plates (m. p. 76°).

0·4192 liberated I = 30·2 c.c. *N*/10 I. Cl as NCl = 12·77.
$C_9H_{11}O_4N_2ClS$ requires Cl as NCl = 12·72 per cent.

2-*Nitrotoluene*-p-*sulphonbenzylamide*,
$NO_2{\cdot}C_6H_3Me{\cdot}SO_2{\cdot}NH{\cdot}CH_2{\cdot}C_6H_5$,
slender, colourless plates with the faintest possible yellow colour (m. p. 94°).

2-*Nitrotoluene*-p-*sulphonbenzylchloroamide*,
$NO_2{\cdot}C_6H_3Me{\cdot}SO_2{\cdot}NCl{\cdot}CH_2{\cdot}C_6H_5$,
crystallises from chloroform, in which it is moderately soluble, in slender, flattened prisms, almost colourless, but with the faintest perceptible shade of yellow (m. p. 144°).

0·3525 liberated I = 20·8 c.c. *N*/10 I. Cl as NCl = 10·46.
$C_{14}H_{13}O_4N_2ClS$ requires Cl as NCl = 10·40 per cent.

Benzene-m-*disulphon*-s-*dimethylamide*, $C_6H_4(SO_2{\cdot}NH{\cdot}CH_3)_2$, small, colourless plates (m. p. 132°).

Benzene-m-*disulphon*-s-*dimethyldichloroamide*,

$SO_2{\cdot}NCl{\cdot}CH_3$

(benzene ring)

$SO_2{\cdot}NCl{\cdot}CH_3$,

crystallises from chloroform, in which it is sparingly soluble, in colourless, transparent prisms (m. p. 135°).

0·3776 liberated I = 45·3 c.c. *N*/10 I. Cl as NCl = 21·26.
$C_8H_{10}O_4N_2Cl_2S_2$ requires Cl as NCl = 21·28 per cent.

When heated rapidly above its melting point, it decomposes violently with blackening.

Naphthalene-1-*sulphonmethylamide*, $C_{10}H_7{\cdot}SO_2{\cdot}NH{\cdot}CH_3$, small, colourless plates (m. p. 137°).

Naphthalene-1-*sulphonmethylchloroamide*, $C_{10}H_7{\cdot}SO_2{\cdot}NCl{\cdot}CH_3$, is very easily soluble in chloroform; it crystallises from a mixture of chloroform and light petroleum in transparent, short, colourless, six-sided prisms (m. p. 78°).

0·3412 liberated I = 25·9 c.c. *N*/10 I. Cl as NCl = 13·45.
$C_{11}H_{10}O_2NClS$ requires Cl as NCl = 13·86 per cent.

Naphthalene-1-*sulphonethylamide*, $C_{10}H_7{\cdot}SO_2{\cdot}NH{\cdot}C_2H_5$, very pale yellow, thick plates (m. p. 93°).

Naphthalene-1-*sulphonethylchloroamide*, $C_{10}H_7{\cdot}SO_2{\cdot}NCl{\cdot}C_2H_5$, crystallises in glittering, transparent, very pale yellow, short prisms terminated by pyramids (m. p. 77°).

0·4602 liberated I = 34·1 c.c. *N*/10 I. Cl as NCl = 13·13
$C_{12}H_{12}O_2NClS$ requires Cl as NCl = 13·14 per cent.

Naphthalene-1-sulphonbenzylamide, $C_{10}H_7\cdot SO_2\cdot NH\cdot CH_2\cdot C_6H_5$, pale yellow, six-sided prisms (m. p. 137°).

Naphthalene-1-sulphonbenzylchloroamide, $C_{10}H_7\cdot SO_2\cdot NCl\cdot CH_2\cdot C_6H_5$, crystallises in short, very pale yellow prisms (m. p. 94°).

0·3534 liberated I = 21·3 c.c. *N*/10 I. Cl as NCl = 10·68.
$C_{17}H_{14}O_2NClS$ requires Cl as NCl = 10·69 per cent.

Naphthalene-2-sulphonmethylamide, $C_{10}H_7\cdot SO_2\cdot NH\cdot CH_3$, thin, colourless plates (m. p. 111°).

Naphthalene-2-sulphonmethylchloroamide, $C_{10}H_7\cdot SO_2\cdot NCl\cdot CH_3$, crystallises in short, colourless prisms (m. p. 91°).

0·3012 liberated I = 23·1 c.c. *N*/10 I. Cl as NCl = 13·59.
$C_{11}H_{10}O_2NClS$ requires Cl as NCl = 13·86 per cent.

Naphthalene-2-sulphonpropylamide, $C_{10}H_7\cdot SO_2\cdot NH\cdot C_3H_7$, colourless, pearly, thin, transparent plates (m. p. 77°).

Naphthalene-2-sulphonpropylchloroamide, $C_{10}H_7\cdot SO_2\cdot NCl\cdot C_3H_7$, crystallises in clusters of glittering, transparent, colourless plates (m. p. 86°).

0·3731 liberated I = 26·3 c.c. *N*/10 I. Cl as NCl = 12·49.
$C_{13}H_{14}O_2NClS$ requires Cl as NCl = 12·49 per cent.

Naphthalene-2-sulphonbenzylamide, $C_{10}H_7\cdot SO_2\cdot NH\cdot CH_2\cdot C_6H_5$, is readily soluble in chloroform, and on adding light petroleum crystallises in small, colourless plates (m. p. 124°).

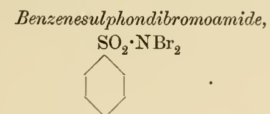
Naphthalene-2-sulphonbenzylchloroamide, $C_{10}H_7\cdot SO_2\cdot NCl\cdot CH_2\cdot C_6H_5$, crystallises in clusters of glittering, transparent, very pale yellow plates (m. p. 117°).

0·4394 liberated I = 25·7 c.c. *N*/10 I. Cl as NCl = 10·37.
$C_{17}H_{14}O_2NClS$ requires Cl as NCl = 10·69 per cent.

The sulphondichloroamides and the sulphonalkylchloroamides are being further studied as they are very reactive and, being easily soluble and very stable, promise to be of considerable value in organic syntheses. Moreover, the sulphondichloroamides are so readily prepared and analysed, and the ease with which they crystallise is so much affected by admixture, that they should prove of considerable use in the investigation of sulphonic acids.

II. *Sulphondibromoamides and Sulphonalkylbromoamides.*

Benzenesulphondibromoamide,



This compound was first prepared by Hoogewerff and van Dorp (*Rec. Trav. Chim.*, 1877, **6**, 373) by dissolving benzenesulphonamide in an excess of alkaline hypobromite and adding acetic acid; a yield of about 60 per cent. of the theoretical was obtained. It can be obtained with much greater ease and in theoretical amount by the action of hypobromous acid on benzenesulphonamide. The best method of procedure is described later. The compound can be obtained perfectly pure, melting at 116°, by one crystallisation from chloroform. A specimen so prepared gave the following numbers on analysis:

0·3874 liberated I = 49·2 c.c. *N*/10 I. Br as NBr = 50·77.
$C_6H_5O_2NBr_2S$ requires Br as NBr = 50·76 per cent.

This and other similar sulphondibromoamides are far more stable towards hydrolysing agents than is usually the case among nitrogen bromides. Two grams of benzenesulphondibromoamide were dissolved in 50 c.c. of 90 per cent. acetic acid and the solution gently boiled for four hours, during which time bromine vapour was very slowly evolved. The solution remained yellow after standing at the ordinary temperature for three days, and on diluting with water about half a gram of pure dibromoamide separated out, the more soluble benzenesulphonamide remaining in solution. Similarly, on boiling 2 grams of the compound with half a litre of water, the melted substance, which at first remained largely undissolved as a heavy oil, slowly dissolved, while a vapour was given off which turned starch paper moistened with potassium iodide blue. After four hours' boiling, the liquid was still yellow, and slowly deposited about 0·4 gram of pure dibromoamide, which crystallised out in large, transparent, yellow plates.

Toluene-p-*sulphondibromoamide,*

$SO_2{\cdot}NBr_2$

CH_3

This compound was prepared by the action of an aqueous solution of hypobromous acid on toluene-*p*-sulphonamide. The following

procedure was adopted in the preparation of this and other similar compounds described in this paper. The finely-powdered sulphonamide was added to a well cooled solution of hypobromous acid * containing about twice the theoretical quantity of the latter and shaken together for some minutes in a large separating funnel; a quantity of chloroform, sufficient to dissolve the sulphondibromoamide, was then added and the shaking continued for a few minutes. To ensure the absence of unchanged sulphonamide, the chloroform solution was again shaken for a short time with a further small quantity of freshly made hypobromous acid solution. The chloroform solution, after separation and drying over fused calcium chloride, deposited the sulphondibromoamide in yellow crystals on driving off the solvent in a current of air. The yield is theoretical. The compound crystallises from chloroform, in which it is moderately soluble, in transparent, orange-coloured plates (m. p. 104°).

0·3192 liberated I = 38·8 c.c. *N*/10 I. Br as NBr = 48·59.
$C_7H_7O_2NBr_2S$ requires Br as NBr = 48·59 per cent.

When the melted substance is heated rapidly, it decomposes explosively, liberating bromine and toluene-*p*-sulphonic bromide.

Potassium toluene-p-*sulphonbromoamide*, $CH_3 \cdot C_6H_4 \cdot SO_2K \colon NBr, 2H_2O$.

This salt can be obtained either directly from the sulphonamide by dissolving it in a warm solution of potassium hydroxide, adding the theoretical quantity of bromine, and cooling, or, more easily, by dissolving finely-powdered toluene-*p*-sulphondibromoamide in a warm 20 per cent. solution of potassium hydroxide and allowing the bright yellow solution to cool. The potassium salt then crystallises out in beautiful, transparent, pale yellow, six-sided plates containing 2 molecules of water of crystallisation.

0·5242 liberated I = 32·2 c.c. *N*/10 I. Br as NBr = 24·56.
$C_7H_7O_2NBrSK,2H_2O$ requires Br as NBr = 24·65 per cent.

When kept for some days over phosphoric oxide in a vacuum, the crystals lose their water of crystallisation and become opaque. The water is also lost when the salt is heated nearly to 100°.

0·4201 of the anhydrous salt liberated I = 29·1 c.c. *N*/10 I. Br as NBr = 27·69.
$C_7H_7O_2NBrSK$ requires Br as NBr = 27·74 per cent.

When heated, the dry salt does not melt, but decomposes with a feeble explosion at about 145—150°.

* This solution was made by shaking bromine with precipitated mercuric oxide suspended in water.

Sodium toluene-p-*sulphonbromoamide*, $CH_3{\cdot}C_6H_4{\cdot}SO_2Na{:}NBr,3H_2O$.

This compound, like the potassium salt, can either be obtained by adding bromine to a solution of the sulphonamide in sodium hydroxide or by dissolving the sulphondibromoamide in a warm 20 per cent. solution of sodium hydroxide. It separates from the warm alkaline solution in long, transparent, pale yellow, flattened prisms, which contain 3 molecules of water of crystallisation.

0·4437 liberated I = 27·3 c.c. *N*/10 I. Br as NBr = 24·60.
$C_7H_7O_2NBrSNa,3H_2O$ requires Br as NBr = 24·51 per cent.

When dried over phosphoric oxide in a vacuum or at 100°, it loses its water of crystallisation, and the crystals, while retaining their outward shape, become opaque.

0·4094 of the anhydrous salt liberated I = 30·1 c.c. *N*/10 I. Br as NBr = 29·39.
$C_7H_7O_2NBrSNa$ requires Br as NBr = 29·38 per cent.

When heated, the anhydrous salt does not melt, but decomposes with a feeble explosion at about 145—150°.

Toluene-o-*sulphondibromoamide*,

$SO_2{\cdot}NBr_2$

CH_3 .

This substance was prepared exactly as the para-derivative; it is readily soluble in chloroform and very slightly in petroleum. When dissolved in warm chloroform and a little warm light petroleum added, it separates, on cooling, in transparent, orange-coloured, four-sided rhombic plates (m. p. 80°).

0·5444 liberated I = 66·2 c.c. *N*/10 I. Br as NBr = 48·62.
$C_7H_7O_2NBr_2S$ requires Br as NBr = 48·59 per cent.

When heated rapidly above its melting point, it decomposes explosively.

Potassium toluene-o-*sulphonbromoamide*, $CH_3{\cdot}C_6H_4{\cdot}SO_2K{:}NBr,H_2O$, was prepared from a 20 per cent. solution of potassium hydroxide; it crystallises in pale yellow, six-sided plates.

0·3370 liberated I = 21·9 c.c. *N*/10 I. Br as NBr = 25·98.

0·2427, when dried for 6 days over phosphoric oxide in a vacuum, lost 0·0135 H_2O. H_2O = 5·56.

$C_7H_7O_2NBrSK,H_2O$ requires Br as NBr = 26·11. H_2O = 5·88 per cent.

When the dry salt is heated, it decomposes at about 130—135°.

Sodium toluene-o-sulphonbromoamide, $CH_3 \cdot C_6H_4 \cdot SO_2Na \colon NBr, H_2O$, was prepared from a 20 per cent. solution of sodium hydroxide; it crystallises in long, slender, pale yellow, flattened prisms.

0·1908 liberated I = 12·9 c.c. *N*/10 I. Br as NBr = 27·03.
$C_7H_7O_2NBrSNa, H_2O$ requires Br as NBr = 27·55 per cent.

This salt loses its water of crystallisation with extreme slowness over phosphoric oxide, but on heating at 100° water is driven off, although the salt also suffers a slight decomposition, as these bromo-derivatives are not so stable as the salts of the chloroamides.

0·3210, when heated at 100° for 2 hours, lost 0·0247 H_2O. H_2O = 7·69.
$C_7H_7O_2NBrSNa, H_2O$ requires H_2O = 6·21 per cent.

When heated, the anhydrous salt does not melt, but decomposes explosively at about 135—140°.

*Nitrobenzene-*m*-sulphondibromoamide*,

$SO_2 \cdot NBr_2$ (benzene ring) NO_2.

In the preparation of this compound, a large quantity of chloroform must be used on account of its sparing solubility. If a small quantity only of the solvent is used, the greater part of the dibromoamide remains undissolved. It is moderately soluble in boiling chloroform and crystallises from the solvent in transparent, orange rhombs, which melt at about 157° with some decomposition, the melted substance reddening and evolving some gas. When rapidly heated to a high temperature, as by placing a small quantity in a melting-point tube into a flame, it decomposes explosively.

0·4382 liberated I = 48·6 c.c. *N*/10 I. Br as NBr = 44·34.
$C_6H_4O_4N_2Br_2S$ requires Br as NBr = 44·41 per cent.

When warmed with solutions of potassium and sodium hydroxides, it dissolves, forming salts which crystallise out, on cooling the solutions, in pale yellow, glittering plates containing water of crystallisation. When anhydrous, they have the composition $NO_2 \cdot C_6H_4 \cdot SO_2[K,Na] \colon NBr$, and decompose explosively when heated.

2-*Nitrotoluene*-p-*sulphondibromoamide*,

$$\begin{array}{c} SO_2\cdot NBr_2 \\ \text{C}_6\text{H}_3 \text{ (ring)}\; NO_2 \\ CH_3 \end{array}$$

This dibromoamide was prepared exactly as the preceding compound, which it closely resembles in solubility and properties. It crystallises from boiling chloroform, in which it is sparingly soluble, in short, orange-coloured, four-sided, transparent prisms; these melt with decomposition at 142—143°.

0·8035 liberated I = 85·4 c.c. $N/10$ I. Br as NBr = 42·49.
$C_7H_6O_4N_2Br_2S$ requires Br as NBr = 42·74 per cent.

When heated quickly to a high temperature, it decomposes explosively; it dissolves in a solution of sodium or potassium hydroxide, forming salts of the monobromoamide, which crystallise in pale yellow plates.

Benzene-m-*disulphontetrabromoamide*, $C_6H_4(SO_2\cdot NBr_2)_2$.

This compound was first prepared with some difficulty by Hoogewerff and van Dorp (*Rec. Trav. Chim.*, 1889, **8**, 173) by adding a dilute solution of silver nitrate to a complex salt, which they obtained as a yellow precipitate on adding acetic acid to a solution of benzene-*m*-disulphonamide in alkaline potassium hypobromite. It also can be prepared quantitatively and with the greatest ease by the action of a solution of hypobromous acid on the amide. On adding a saturated aqueous solution of benzene-*m*-disulphonamide to an excess of a well cooled solution of hypobromous acid, benzene-*m*-disulphontetrabromoamide separates almost at once as an orange-yellow, crystalline powder, which can be filtered off, washed, and dried, first by pressing between filter paper, and finally over phosphoric oxide in a vacuum. The following analysis of a specimen so prepared shows that it is perfectly pure.

0·3370 liberated I = 48·8 $N/10$ I. Br as NBr = 57·89.
$C_6H_4O_4N_2Br_4S_2$ requires Br as NBr = 57·93 per cent.

The compound may be recrystallised from chloroform, in which it is sparingly soluble.

Naphthalene-2-sulphondibromoamide,

$C_{10}H_7 \cdot SO_2 \cdot NBr_2$.

This compound crystallises from warm chloroform, on adding a little light petroleum, in deep orange-coloured, four-sided plates. It melts with decomposition and evolution of gas at 90—95°.

0·3550 liberated I = 38·6 c.c. *N*/10 I. Br as NBr = 43·47.
$C_{10}H_7O_2NBr_2S$ requires Br as NBr = 43·80 per cent.

It dissolves in warm solutions of potassium and sodium hydroxides, forming salts of the monobromoamide which crystallise in small, pale yellow plates.

Arylsulphonalkylbromoamides.

The sulphonalkylbromoamides are very easily prepared by shaking a chloroform solution of the sulphonalkylamide with an excess of an aqueous solution of hypobromous acid and proceeding as before described. The presence of free bromine is best avoided, and when preparing compounds containing ethyl or benzyl a little precipitated mercuric oxide may with advantage be added to the solution of hypobromous acid, the chloroform solution of the bromoamide being filtered from this at the pump previous to separating and drying. It is also generally advisable to ensure the complete conversion of the amide by shaking a second time for a few minutes with freshly prepared hypobromous acid. A number of typical compounds have been prepared. The methyl compounds are the most stable and may be kept for a long time unchanged; the benzyl derivatives, on the other hand, rapidly decompose, even over phosphoric oxide, and when light is excluded. On heating strongly above their melting points, they all decompose with reddening and evolution of gas.

Benzenesulphonmethylbromoamide, $C_6H_5 \cdot SO_2 \cdot NBr \cdot CH_3$.—This compound is sparingly soluble in chloroform; it crystallises in beautifully brilliant, transparent, pale yellow plates, which appear to be flattened rhombs (m. p. 107°).

0·5338 liberated I = 42·7 c.c. *N*/10 I. Br as NBr = 31·98.
$C_7H_8O_2NBrS$ requires Br as NBr = 31·97 per cent.

Benzenesulphonbenzylbromoamide, $C_6H_5 \cdot SO_2 \cdot NBr \cdot CH_2 \cdot C_6H_5$.—This compound crystallises in clusters of very pale yellow, four-sided prisms (m. p. 104°). On heating above its melting point, it decomposes with reddening and effervescence at about 140°.

0·3805 liberated I = 23·4 c.c. *N*/10 I. Br as NBr = 24·59.
$C_{13}H_{12}O_2NBrS$ requires Br as NBr = 24·52 per cent.

It slowly decomposes, even when kept excluded from the light in a dry atmosphere. To gain a rough idea of the rapidity of this change, a quantity of the pure compound was placed in a desiccator over phosphoric oxide. After two days, it had obviously slightly decomposed, a smell resembling benzaldehyde was noticed, and on analysis the percentage of Br as NBr was found to be 24·05 per cent.

Toluene-p-*sulphonmethylbromoamide*, $CH_3·C_6H_4·SO_2·NBr·CH_3$.—This compound crystallises from warm chloroform on adding a little petroleum in pale yellow, apparently four-sided prisms (m. p. 112°). When heated above its melting point, it decomposes with reddening and effervescence at about 160°.

0·4810 liberated I = 36·6 c.c. *N*/10 I. Br as NBr = 30·42.
$C_8H_{10}O_2NBrS$ requires Br as NBr = 30·27 per cent.

Toluene-p-*sulphonethylbromoamide*, $CH_3·C_6H_4·SO_2·NBr·C_2H_5$.—This compound crystallises in bright yellow, glittering, transparent, four-sided prisms (m. p. 113°). On heating further, it decomposes with reddening and evolution of gas at about 150°.

0·4856 liberated I = 35·1 c.c. *N*/10 I. Br as NBr = 28·89.
$C_9H_{12}O_2NBrS$ requires Br as NBr = 28·74 per cent.

Toluene-p-*sulphonbenzylbromoamide*, $CH_3·C_6H_4·SO_2·NBr·CH_2·C_6H_5$.—This compound forms clusters of transparent, four-sided, rhombic plates, having an exceedingly pale yellow colour; its solution in chloroform is, however, distinctly yellow. It melts at 149°. On heating a few degrees higher to about 156°, it decomposes with reddening and evolution of gas.

0·6705 liberated I = 39·4 c.c. *N*/10 I. Br as NBr = 23·49.
$C_{14}H_{14}O_2NBrS$ requires Br as NBr = 23·50 per cent.

Nitrobenzene-m-*sulphonmethylbromoamide*,

$SO_2·NBr·CH_3$

NO_2

—This compound crystallises from chloroform, in which it is moderately soluble, in transparent, pale yellow, four-sided rhombic plates (m. p. 149°). When heated strongly, it decomposes with reddening and evolution of gas about 180°.

0·4923 liberated I = 33·2 c.c. *N*/10 I. Br as NBr = 26·96.
$C_7H_7O_4N_2BrS$ requires Br as NBr = 27·09 per cent.

Nitrobenzene-m-*sulphonbenzylbromoamide*,

$NO_2 \cdot C_6H_4 \cdot SO_2 \cdot NBr \cdot CH_2 \cdot C_6H_5$.

—This compound is moderately soluble in warm chloroform, forming a distinctly yellow solution, from which it crystallises in clusters of very slender prisms having a faint yellow colour ; it melts at 147°.

0·3959 liberated I = 21·4 c.c. *N*/10 I. Br as NBr = 21·61.

$C_{13}H_{11}O_4N_2BrS$ requires Br as NBr = 21·54 per cent.

2-*Nitrotoluene*-p-*sulphonmethylbromoamide*,



—This substance crystallises from warm chloroform, in which it is moderately soluble, in yellow, transparent, short, six-sided prisms ; it melts at 117°. When heated further it darkens, becomes red, and decomposes with evolution of gas at about 180°, as does also the ethyl compound.

0·5158 liberated I = 33·2 c.c. *N*/10 I. Br as NBr = 25·73.

$C_8H_9O_4N_2BrS$ requires Br as NBr = 25·86 per cent.

2-*Nitrotoluene*-p-*sulphonethylbromoamide*,

$NO_2 \cdot C_6H_3Me \cdot SO_2 \cdot NBr \cdot C_2H_5$.

—This compound crystallises in glittering, transparent, pale yellow rhombs (m. p. 96°).

0·5774 liberated I = 35·9 c.c. *N*/10 I. Br as NBr = 24·86.

$C_9H_{11}O_4N_2BrS$ requires Br as NBr = 24·74 per cent.

2-*Nitrotoluene*-p-*sulphonbenzylbromoamide*,

$NO_2 \cdot C_6H_3Me \cdot SO_2 \cdot NBr \cdot CH_2 \cdot C_6H_5$.

—This compound crystallises from chloroform, in which it is only sparingly soluble, in clusters of extremely slender, flattened prisms, having a very faint yellow colour (m. p. 151°).

0·4421 liberated I = 23·1 c.c. *N*/10 I. Br as NBr = 20·89.

$C_{14}H_{13}O_4N_2BrS$ requires Br as NBr = 20·76 per cent.

Benzene-m-*disulphon*-s-*dimethyldibromoamide*,

$$C_6H_4(SO_2\cdot NBr\cdot CH_3)_2$$

—This compound crystallises from chloroform, in which it is sparingly soluble, in very pale yellow, four-sided plates.

0·3744 liberated I = 35·3 c.c. *N*/10 I. Br as NBr = 37·69.
$C_8H_{10}O_4N_2Br_2S_2$ requires Br as NBr = 37·87 per cent.

It melts at 176° with slight reddening; if maintained at this temperature for a few seconds, or heated a few degrees higher, it decomposes, becoming deep red in colour and liberating bubbles of gas.

Various reactions of the sulphondibromoamides and of the sulphonalkylbromoamides are being studied.

The author's thanks are due to the Government Grant Committee of the Royal Society for a grant in aid of the work described in this paper, and to A. Gordon Salamon, Esq., for the gift of a large quantity of pure toluene-*o*- and -*p*-sulphonic chlorides.

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XX.—*Theory of the Production of Mercurous Nitrite and of its Conversion into Various Mercury Nitrates.*

By PRAFULLA CHANDRA RÂY.

WHEN mercury and dilute nitric acid are left together for a long time, the following salts may form: (1) $Hg_2(NO_2)_2$, (2) $Hg(NO_2)_2$, (3) $Hg_2(NO_3)_2,2H_2O$, (4) $HO\cdot Hg_2NO_3$, (5) $Hg_2(NO_3)_2,HO\cdot Hg_2NO_3$, (6) $Hg_2(NO_3)_2,4HO\cdot Hg_2NO_3$, (7) $HgO,2HO\cdot Hg_2NO_3$, (8) $HgO,HO\cdot HgNO_3,HO\cdot Hg_2NO_3$, (9) $Hg(NO_3)_2$,aq., (10) $HO\cdot HgNO_3$. Some of these have not, indeed, been isolated in this way, but doubtless exist in the solution. Analyses of the mother liquors of mercurous nitrite (1) and of the hydroxy-mercurosic nitrates (7 and 8) indicate that, throughout the successive production of the salts just enumerated, it is mercurous nitrite which gives rise to the

production of, first, normal mercurous nitrate (3), then the hydroxy-mercurous salts (4, 5 and 6), and, lastly, the mercurosic (7 and 8) and mercuric salts (9 and 10).

(1) *Mercurous Nitrite*, $Hg_2(NO_2)_2$ (Trans., 1897, 71, 337).—When mercury is covered with nitric acid (sp. gr. 1·11/15°) to a depth of 10 cm. at 30—35°, the bright yellow mercurous nitrite soon begins to crystallise, generally as a crust over the mercury, but sometimes in separate large crystals. The whole may be left undisturbed for about 50 hours without the crystals showing erosion. Very little nitric oxide forms on the mercury and even that is soon absorbed by the solution. In 24 hours, the solution just over the mercury has attained a sp. gr. of 1·6—1·7, whilst at the surface its sp. gr. is hardly altered, scarcely any mercury salts being present.

The following mode of procedure was adopted in collecting for analysis the mother liquor of mercurous nitrite immediately in contact with the mercury. About 340 grams of mercury were put into a tall beaker, 10 cm. in diameter, on the bottom of which they formed a crescentic or annular pool. A mixture of 600 c.c. of water and 150 c.c. of nitric acid (sp. gr. 1·43/15°) was added and gave a depth of dilute acid of 10 cm. The yield of mercurous nitrite was about 16 grams in 24 hours. In a broader vessel, using the same quantity of dilute acid, which then had a depth of only 5 cm., about one-third less nitrite per unit surface of mercury was obtained in the same time. The mother liquor was slowly and steadily withdrawn for analysis by means of a graduated pipette held against the bottom of the beaker, where it was not covered by the mercury. Total nitrogen was estimated by the Crum-Frankland process, and nitritic nitrogen by the interaction with urea, following P. F. Frankland's method. One c.c. of solution was mixed with excess of pure sodium hydroxide, heated to boiling, and, after cooling, made up with water to 100 c.c. Of the solution, clarified by standing or filtration, aliquot portions were taken for the nitrogen determinations. The mercury of the mercurous salts was weighed as chloride and the rest as sulphide. The results are shown in the table on p. 173.

Notes to the Tabulated Results.—I*a* is slightly abnormal,* V*a*, red nitric acid was used; VI*a*, some mercurous nitrite was added at the beginning; VII, VIII, and IX, stoppered bottles were employed in place of covered beakers; V and IX differed only as to temperature.

Mercurous nitrite is the product of the combined action of nitrous and nitric acids on mercury: $2Hg + NO_2{\cdot}H + HO{\cdot}NO_2 = Hg_2(NO_2)_2 + H_2O$. Some of the nitrite is decomposed by the nitric acid, the quantity of nitrous acid thus rapidly growing, until mercurous nitrite and nitrate are accumulating in molecular proportions. From this time, the

* The acid used was evidently a little stronger than in other experiments.

Reference No.	Laboratory temperature.	Duration of experiment in hours.	Atoms per 1000 molecules of water. Mercury. Total.	Mercury. Mercuric.	Nitrogen. As nitrate.	Nitrogen. As nitrite.	Nitrogen. As free acid.	Ratio of total to nitritic.
	(1)	(2)	(3)	(4)	(5)	(6)	(7)	(8)
I	35°	2	51·0	5·6	26·0	25·0	66·0	4·66
I*a*	35	26	52·5	5·4	24·5	28·0	69·5	4·4
II	34	3	53·0	6·5	30·0	23·0	55·0	4·64
III	33	2	60·0	6·0	37·0	23·0	35·0	4·2
IV	33	48	67·0	3·0	48·0	19·0	20·0	4·55
IV*a*	33	96	67·0	8·0	43·0	24·0	28·0	3·92
V	26	2	40·5	2·5	22·5	18·0	36·5	4·3
V*a*	26	$1\frac{2}{3}$	40·5	2·5	22·5	18·0	36·5	4·3
VI	23	24	58·5	8·0	35·5	23·0	41·5	4·36
VI*a*	23	24	58·5	7·0	35·5	23·0	41·0	4·27
VII	23	$1\frac{1}{2}$	35·8	2·0	23·5	15·0	30·5	4·73
VIII	23	$3\frac{1}{2}$	42·0	2·0	26·0	16·0	34·0	5·0
IX	23	$3\frac{3}{4}$	42·0	2·5	26·5	15·5	33·0	5·0
X	22	$1\frac{1}{2}$	38·5	2·0	23·5	15·0	35·5	5·0
Nitric acid...	15	—	—	—	63·5	—	63·5	—

nitrous acid in the solution remains constant in quantity. It has become the catalytic agent between the nitric acid and the mercury, which now interact in the following manner: $4Hg + 4HNO_3 = Hg_2(NO_2)_2 + Hg_2(NO_3)_2 + 2H_2O$. In accordance with this equation, it will be seen that in Expt. I there were 25 mols. of nitrite to 26 of nitrate, and in I*a* 28 to 24·5. In Expt. II there were 23 mols. of nitrite to 30 of nitrate, showing a falling off of nitrite, and after that a still greater decrease. At lower temperatures, the effects of diffusion and crystallisation were enough to mask the equal production of nitrite and nitrate.

An interesting point, deducible from the composition of the mother liquor, is that of the rapid diffusion of the nitric acid into the layer of solution next to the mercury. In every case, the proportion of nitrogen to water in the solution next to the mercury was found to exceed that in the dilute acid used, notwithstanding the fact that the solution had already parted with much nitrogen in the form of mercurous nitrite. This was most striking in the experiments at 35°. The ratio of nitratic to nitritic nitrogen is also remarkable, being just 4 at 22—23°, and not less than 3 at other temperatures.

(2) *Mercuric Nitrite.*—When mercurous nitrite is dissolved in hot

water, about 20 per cent. of it is resolved into mercuric nitrite and mercury (Trans., 1897, **71**, 340). When dissolved in its nitrate mother liquor, it will behave similarly, except that mercury, instead of being set free, will now occur as mercuric salt in presence of the nitrous and nitric acids, $Hg_2(NO_2)_2 + HNO_2 + HNO_3 = 2Hg(NO_2)_2 + H_2O$. The presence of mercuric salts in the solution is thus explained.

(3) *Normal Mercurous Nitrate.*—When the nitric acid used is of sp. gr. 1·135—1·14 instead of only 1·11, small, soft crystals appear in one or two days, along with those of mercurous nitrite, but soon give place either to a crystalline crust or to large, isolated crystals of $Hg_2(NO_3)_2,2H_2O$. The stronger acid has, in this case, converted more of the nitrite into nitrate.

(4, 5 and 6) *The Hydroxy-mercurous Nitrates*: $HO{\cdot}Hg_2NO_3$ and *Marignac's Two Salts* $Hg_2(NO_3)_2,HO{\cdot}Hg_2NO_3$ and $Hg_2(NO_3)_2,4HO{\cdot}Hg_2NO_3$.—Mercurous nitrite, by changing into mercuric nitrite, also becomes the source of the hydroxide of the basic mercurous nitrates, for mercuric nitrite is readily hydrolysed into basic salt (Trans., 1904, **85**, 523). Acting on mercurous nitrate, this hydroxy-mercuric nitrite becomes mercurous nitrite again and hydroxy-mercuric nitrate (10), while there is a slow escape of nitric oxide from the hydrolysing mercuric nitrite. So long as any mercury remains, the hydroxy mercuric nitrate combines with it as hydroxy-mercurous nitrate (4). Omitting intermediate stages, the result may be formulated as $2Hg_2(NO_3)_2 + 3Hg + Hg(NO_2)_2 + 2H_2O = 4HO{\cdot}Hg_2NO_3 + 2NO$. But the hemihydroxy-salt (4) separates out only in combination with normal nitrate. In the course of several weeks, all the mercurous nitrite disappears and large crystals of the 5/3-hydroxy-mercurous nitrate (6) are deposited. Where the temperature is not much above 22°, these crystals are for a time accompanied or preceded by those of the 4/3-hydroxy-mercurous nitrate (5), either as elongated tables and prisms or looking like glass wool. But this salt is ultimately all replaced by the 5/3-salt (6).

(7 and 8) *α- and β-Hydroxy-mercurosic Nitrates.*—Both salts were partly described in the 1897 paper (Trans., *loc. cit.*), but were there represented as being basic nitrites. The α-hydroxy-mercurosic nitrate, $Hg''O,2HO{\cdot}Hg_2NO_3$, occurring in orange-yellow, hard, apparently crystalline nodules, is a new salt. The β-salt (8),

$$Hg''O,HO{\cdot}Hg''NO_3,HO{\cdot}Hg_2NO_3,$$

forms tufts and star-like aggregates of thin, lemon-yellow plates. It was mistaken by Lefort (*Compt. rend.*, 1845, **20**, 1300) for mercurous nitrite, which it resembles; its real nature was made out by Gerhardt (*Compt. rend.*, 1848, **26**, 432). Both salts may be viewed as normal orthonitrates (compare Hartley, Trans., 1903, **83**, 662). They are both obtainable from the aqueous solution of mercurous nitrite, but only the β-salt from the solution of mercury in nitric acid. When

the mother liquor of mercurous nitrite, after this salt has ceased to separate, is left in a flat dish to evaporate, the α-salt begins to appear. Some days later, the temperature varying from 22—25°, the deposition of this salt is complete and the crystallisation of the β-salt begins. In about two weeks from the time when the α-salt appears, the deposition of the β-compound is also finished. With the first appearance of the α-salt, the solution becomes acid, the acidity increasing as the salts separate. Throughout this period, an odour of nitrous acid is observable, arising no doubt from aërial oxidation of nitric oxide. After boiling mercurous nitrite with water, when nitric oxide freely escapes, its mother liquor goes much more rapidly through the above changes on evaporating it at a gentle heat. Two analyses of the solution were made. Just before it commenced to deposit the β-salt, it was found that to 1000 mols. of water in the liquid there were 0·055 atom of mercury and 0·147 atom of nitrogen. The proportions of the salts were approximately 1 mol. of mercurous nitrite and 5 mols. each of mercuric nitrite, mercuric nitrate, and nitrous acid. In the final mother liquor of the salt were found, to 1000 mols. of water, 0·076 atom of mercury (all mercuric) and 0·165 atom of nitrogen (7/90ths in the form of free acids and more than 2/3rds as nitritic nitrogen). It will be seen, therefore, that the salt is deposited so long as the proportion of mercurous nitrate is large enough. The stability of mercuric nitrite in the acid mother liquor is remarkable; it is much less marked in absence of acid (Trans., 1904, *loc. cit.*).

As regards the formation of the mercurosic nitrates, if mercuric nitrite were fully decomposed into mercuric oxide and nitrous anhydride the result would be $3Hg(NO_2)_2 = 4NO + 3HgO,N_2O_5$. But, since some of the mercuric nitrate will interact with mercurous nitrite, also present, to regenerate mercurous nitrate and mercuric nitrite, the above equation may be re-written, either as $Hg(NO_2)_2 + 2Hg_2(NO_2)_2 = 4NO + HgO,2Hg_2O,N_2O_5$ (anhydrous α-salt) or $2Hg(NO_2)_2 + Hg_2(NO_2)_2 = 4NO + 2HgO,Hg_2O,N_2O_5$ (anhydrous β-salt).

Analyses of the β-salt have fully identified it with the Lefort-Gerhardt salt. There is some difficulty in getting the α-salt pure; it is liable to be contaminated either with mercurous nitrite, at first, or with the β-salt afterwards. It is better to take the later-formed orange-coloured nodules of the salt, since these can be brushed clean from the brittle β-salt. The first preparation was obtained by the slow method in the cold, whilst the second was produced by hot evaporation.

	Found.		Calculated.
Mercurous mercury	66·69	67·98	68·14
Mercuric mercury	17·38	17·12	17·04
Nitrogen	2·65	2·44	2·38

The formation of β-hydroxy-mercurosic nitrate from a solution of mercury in nitric acid of sp. gr. 1·11 or 1·2 alternates with that of the 4/3-hydroxy-mercurous nitrate (p. 174). In warmer weather (35°), the mercurosic salt is deposited, in colder (22°), the mercurous salt. With change of temperature, the one salt dissolves and the other separates. To prepare the mercurosic salt, about 345 grams of mercury and 750 c.c. of nitric acid (sp. gr. 1·11) are occasionally shaken together until no mercury or mercurous nitrite remains. Within two months, beautiful, lemon-yellow clusters and rosettes of the β-hydroxy-mercurosic nitrate appear, if the temperature is high enough, otherwise, only hydroxy-mercurous nitrate is obtained. When the solution begins to yield the yellow salt, the nitrogen present in it is in the form of 11 atoms as mercurous nitrite, 18·3 atoms as hemihydroxy-mercuric nitrate (a soluble salt), and a very little more as free acids, to 1000 mols. of water. These proportions are closely expressed by the proportion $10HO\cdot HgNO_3$ to $3Hg_2(NO_2)_2$. After all the mercurosic nitrate had been deposited, the solution, no longer basic, contained, to 1000 mols. of water, 9·8 atoms of nitrogen as mercurous nitrite and 39·2 atoms as normal mercuric nitrate, besides a very little as free acids : $8Hg(NO_3)_2$ to $Hg_2(NO_2)_2$. The above solutions were obtained for analysis in separate experiments, and confirmatory results were also obtained in other experiments. It may be deduced from these analyses that the hydroxy-mercurosic nitrate was derived exclusively from mercurous nitrite and nitrate in the way explained.

The 4/3-hydroxy-mercurous nitrate and the β-hydroxy-mercurosic nitrate may be quickly obtained as follows : 50 grams of mercury and 75 grams of nitric acid (sp. gr. 1·2) are digested together, at first in the cold and then at a gentle heat. After some time, the solution becomes permanently yellow and deposits the β-hydroxy-mercurosic nitrate, which must be removed while the solution is hot, since it dissolves when the solution is allowed to cool, being replaced by the 4/3-hydroxy-mercurous nitrate. On heating the solution, this disappears, and the yellow salt reappears. By repeating the above experiment in an atmosphere of carbon dioxide, it was found that air plays no part in the formation of a mercuric nitrate.

(9 and 10) *Normal and Hydroxy-mercuric Nitrates.*—The occurrence of normal mercuric nitrate along with mercuric nitrite in the final mother liquor, as well as its origin from mercurous nitrite, has been already described. The presence of hydroxy-mercuric nitrate in the solution which deposits β-hydroxy-mercurosic nitrate has also been pointed out and explained.

For assistance in arranging the matter in this paper, the author is

deeply indebted to Dr. Edward Divers, F.R.S. ; indeed, it is not too much to say that, but for his unremitting labour and ungrudging help, it could not have appeared in its present shape.

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XXI.—*The Nitrites of the Alkali Metals and Metals of the Alkaline Earths and their Decomposition by Heat.*

By PRAFULLA CHANDRA RÂY.

Barium Nitrite.—After I had completed my work on this salt, my attention was drawn to an elaborate paper on the subject by Arndt (*Zeit. anorg. Chem.*, 1901, **27**, 341), which also contains a full historical summary. I shall therefore confine myself to such information as is supplementary to this author's statements.

I am in a position to confirm Arndt as regards his inability to obtain pure barium nitrite by N. W. Fischer's method. Repeated crystallisations from alcohol gave a product which was always contaminated with 10 to 12 per cent. of the nitrate.

Barium nitrite was therefore prepared by double decomposition between silver nitrite and barium chloride in molecular proportions. As a solution of this salt has been found to be perfectly stable when heated to boiling or evaporated on the water-bath, the precautions adopted in the case of the preparation of mercuric nitrite (Trans., 1904, **85**, 523) were quite unnecessary. Hot saturated solutions of the components were mixed together and vigorously agitated in a stoppered bottle in order to bring about the coagulation of silver chloride, the clear filtrate was evaporated nearly to dryness and allowed to crystallise, when clusters of glistening, faintly yellow needles slowly separated ; these were pressed between folds of blotting paper and analysed in the usual way.

Found Ba = 55·42 ; $Ba(NO_2)_2,H_2O$ requires Ba = 55·46 per cent.

If the evaporation of the solution is carried further either on the water-bath or under diminished pressure over sulphuric acid, an efflorescent, white, granular mass is obtained. The whole of the water of crystallisation cannot be driven off even if the salt be powdered finely and dried in the steam oven. A sample thus dried gave

Ba = 58·91 per cent., the calculated amount for $Ba(NO_2)_2$ being 59·8, whilst that for $Ba(NO_2)_2,\frac{1}{2}H_2O$ is 57·56 per cent. Arndt's product, a "snow-white powder," was probably slightly dehydrated by the absolute alcohol used in its production, and this may account for the white, powdery appearance; his analysis also would seem to bear this out, as he found Ba = 56·86 per cent.

Calcium Nitrite.—This salt was prepared in a manner similar to that employed for its barium analogue. The solution could be evaporated on the water-bath without the salt becoming either decomposed or partially converted into nitrate. Owing to its highly deliquescent character, considerable difficulty was experienced in obtaining the salt in a form fit for analysis. When the concentrated solution was kept in a desiccator a yellow, pasty, crystalline mass was secured, which was found to contain rather more water than that required by the formula $Ca(NO_2)_2,H_2O$. When it was allowed to remain longer in the desiccator, the salt rapidly effloresced and ultimately turned into a hard lump, which did not lose in weight when heated on the water-bath; it gave off moisture, however, when heated in a bulb-tube, and yielded 27·03 per cent. of calcium, the theory for $Ca(NO_2)_2,\frac{1}{2}H_2O$ being 28·37. It is thus very probable that a semi-hydrated stable salt actually exists. The behaviour of the barium salt also points to the same conclusion.

Potassium and Sodium Nitrites.—These compounds were also prepared by double decomposition between silver nitrite and the respective chlorides. As already pointed out by Divers (Trans., 1899, **75**, 86), solutions of the alkali nitrites can safely be evaporated on the water-bath. The nitrites were found to be free from nitrates. According to Lang (*J. pr. Chem.*, 1862, **86**, 296), potassium nitrite crystallises with one molecule of water, whilst Divers found his crystals to be perfectly anhydrous. My own analyses go to confirm the latter chemist. I picked out small crystals, which were powdered and pressed between folds of blotting paper. An analysis gave 1·8 and 44·94 per cent. of moisture and potassium respectively, the calculated value for potassium nitrite being 45·88.

Magnesium Nitrite.—An aqueous solution of this salt was prepared by double decomposition between barium nitrite and magnesium sulphate; it could not, however, be evaporated on the water-bath, as it was found that nitric oxide was evolved with consequent formation of a basic nitrate. The solution was therefore concentrated under diminished pressure over sulphuric acid, when a crystalline, very faint yellow crust was obtained, which was pressed between folds of blotting paper in order to remove the adhering mother-liquor. The substance dissolved to a clear solution, and, on analysis, gave Mg = 14·72; the formula $Mg(NO_2)_2,3H_2O$ required Mg = 14·12 per cent.

If this salt, instead of being removed at the above stage, is allowed to remain in the desiccator, it loses its lustre, and is converted into a hard, efflorescent, white mass. As the exact composition of this substance has been a matter of some controversy, three distinct preparations were undertaken, the properties and the analyses of which are given below.

1*st Preparation.*—In this case, complete solution of the substance in water was not obtained, but there was a slight residue : 0·345 gave 0·238 $Mg_2P_2O_7$ from the soluble, and 0·0115 $Mg_2P_2O_7$ from the insoluble portions; whence Mg = 14·92 and 0·72 per cent. respectively, the theoretical value for $Mg(NO_2)_2,2H_2O$ being 15·78.

2*nd Preparation.*—The substance dissolved with a faint opalescence. Analysis gave Mg = 16·30 ; N = 18·46 ; the calculated values being Mg = 15·78, N = 18·42 per cent. respectively.

3*rd Preparation.*—The salt dissolved just as above, and gave Mg = 16·27 per cent.

The nitrogen, as estimated by the Crum-Frankland method, was the same in amount as when measured by the "urea" process.

Magnesium nitrite, like the foregoing nitrites, is a deliquescent salt ; it crystallises with 3 mols. of water, of which it loses only 1 mol. if it is not removed from the desiccator at this stage. The dehydration cannot be carried further, and in this form it has been found to be stable, whereas the crystalline salt, when it is stored in a stoppered bottle, slowly decomposes, evolving nitrous fumes. In this respect, magnesium nitrite bears a marked analogy to mercuric nitrite (Trans., 1904, **85**, 524).

It is thus evident that the experiences of Lang, who analysed only the crystalline variety (*J. pr. Chem.*, *loc. cit.*), and of Hampe, who examined it in the dehydrated form only (*Annalen*, 1863, **125**, 334), are fully borne out, whereas Vogel (*Zeit. anorg. Chem.*, 1903, **35**, 398) appears to be partially correct when he states that the salt, when dehydrated as above, undergoes slight decomposition like the chloride.

Divers has already drawn attention to the fact that a solution of the alkali nitrites can safely be evaporated even at the boiling temperature without decomposing or oxidising it (Trans., 1900, **75**, 86). Not only has this observation been found to hold good as regards the sodium and potassium nitrites, but it can be extended equally to solutions of barium and calcium nitrites. It is often stated that a solution of sodium nitrite gradually absorbs oxygen from the air.* I have, however, allowed solutions of this compound to evaporate spontaneously in a flat dish for two months at temperatures varying from 25° to 30°, and have tested them from time to time without being able to detect any appreciable oxidation to the nitrate. Even the

* "Nimmt langsam in Lösung Sauerstoff auf" (Lang, *loc. cit.*, p. 296).

crystalline crust which was deposited has been found to be a pure nitrite. Sodium and potassium nitrites are distinctly, although faintly, yellow, and give markedly yellow concentrated aqueous solutions (compare Divers, Proc., 1900, **16**, 70).

Both Arndt and Vogel agree in stating that a concentrated solution of barium nitrite has a yellow tint, whilst the latter also makes the same observation with regard to calcium nitrite solution; but these chemists seem not to have noticed that these nitrites in the solid form also have a distinct pale yellow colour. They prepared the salts by precipitation from concentrated solution by alcohol, and thus obtained them as "white powders," but this appearance was probably due to the fine state of division in which these compounds were produced.

Summarising the results, it may be laid down that, in the first and second groups of the periodic system, the higher the atomic weight of the element the more pronounced is the colour of its nitrites. Mercurous nitrite stands at the head of the series, being markedly yellow, while silver nitrite occupies an intermediate position between this compound and the nitrites of sodium and potassium. In the second group also, although the colour is much less developed than in the first, barium nitrite stands at the head of the series, calcium nitrite comes next, whilst magnesium nitrite occupies the lowest place.*

As regards stability also, magnesium nitrite ranks lowest in position in the present series. This might be expected from the feebly basic properties of the magnesium oxide; in fact, this element forms a connecting link, as it were, between barium, strontium, and calcium on the one hand, and cadmium and zinc on the other.

A dilute solution of magnesium nitrite was kept for six months in a stoppered bottle, which was opened from time to time; the salt was found to remain perfectly stable. The solution, however, cannot be evaporated on the water-bath, as it undergoes partial decomposition, even at 60°, with evolution of nitric oxide.

Decomposition of the Nitrites by Heat [with ATUL CHANDRA GAÑGULI, B.A.].

The substance was placed in a combustion tube of Jena glass which was attached to a glass spiral, $1\frac{1}{2}$ metres in length, packed close

* Strictly speaking, mercury occupies a two-fold position in the Periodic System. On account of the close similarity in properties between mercurous nitrite and its silver analogue, as has been pointed out in some of my previous communications, these two metals should be placed side by side. But mercuric nitrite, on the other hand, strongly resembles magnesium nitrite, justifying the position assigned to it by Mendeléef, and it is interesting to note that it has a pale yellow colour, more pronounced than that of the barium compound.

with glass beads which had been previously soaked in a strong caustic potash solution free from nitrite or nitrate. The apparatus, which in fact was a modified and improved form of that used in a similar experiment with mercuric nitrite (Trans., 1904, **85**, 525), was then exhausted with the aid of the mercury pump. The heating was effected with a Bunsen burner in two distinct stages, which are termed the "initial" and the "final" stages respectively. In the first stage, the salt was heated slowly aad gently for about 15 minutes, keeping the temperature, as far as practicable, a little above the fusion point; for instance, in the case of the barium nitrite, the temperature was between 250° and 300°, the melting point of this salt being about 220° (Arndt). At the end of the operation, the temperature was much lowered, so that no more gas was evolved. In the second stage, a far stronger heat was applied, the temperature rising to 450° and 500°. The gases which were absorbed by the caustic potash, either as nitrite or nitrate or both, were analysed, as were also those which collected in the reservoir of the mercury pump.

Barium Nitrite.—Expt. I. The substance (0·341 gram) turned distinctly yellow and remained so as long as the heating was continued and effervesced with intumescence. No nitrous fumes were noticed; the gas consisted of 19·2 c.c. of nitric oxide* and 5·0 c.c. of nitrogen. Besides baryta, the residue contained a mixture of nitrate and nitrite, the total nitrogen being 21·0 c.c., of which 13·3 c.c. was in the form of nitrite. The caustic potash of the glass beads yielded 1·8 c.c. of nitrogen in the form of pure nitrite.

The sum total of nitrogen in the salt (in the moist state) at 33° and 752 mm. was thus made up of the following: as gas, 14·6 c.c.; in the residue, 21·0 c.c.; in the caustic potash, 1·8 c.c.; the total being 37·4 c.c., whence the nitrogen found was 0·0397, the calculated amount being 0·040. It would thus appear that the method of analysis was fairly trustworthy, and that nearly 25 per cent. of the nitrogen in the salt was given off as nitric oxide. The ratio in volume of the nitrogen in the residue as nitrate to nitrite was as 1:1·73.

Expt. 2. Salt taken, 0·255 gram.

1st Stage. NO = 19·6 c.c; N = 3·4 c.c.; $t = 30°$; $p = 759$ mm., whence N as NO = 0·0105 gram, the total nitrogen in the salt being 0·03 gram; thus 29·28 per cent. of the nitrogen was given off as nitric oxide.

2nd Stage. Nitrous fumes were noticed and 4·6 c.c. of gas were collected; these were almost completely absorbed by an alkaline solution of pyrogallate.

For the sake of comparison, a blank experiment was made by heating barium nitrate directly at about 500° for two minutes;

* A strong solution of ferrous sulphate was used as the absorbent for this gas.

2 c.c. of gas were collected, which proved to be oxygen. It should not, however, be supposed that the reaction in this case is so simple as that represented by the equation: $Ba(NO_3)_2 = Ba(NO_2)_2 + O_2$. On examining the liquid in the worm receiver, a small quantity of a mixture of nitrate and nitrite was obtained. Here also the reactions as detailed below probably take place, only in the reverse order.*

Calcium Nitrite.—Expt. 1. Salt = 0·1386 gram.

1st Stage. NO = 25·2 c.c.; N = 1·8 c.c. at 29° and 756 mm.

2nd Stage. Gas = 3 c.c. (completely absorbed by alkaline pyrogallate). The residue was found to be only lime, free from nitrite or nitrate. Analysis of the liquid distillation gave; total N = 11·2 c.c.; as nitrite = 8·05 c.c.

The total nitrogen in the salt is thus made of 3 parts: as NO = 12·6 c.c.; as N = 1·8 c.c.; in the alkaline liquid = 11·2 c.c.; whence N (found) = 0·02772 gram; N (calc.) = 0·0277 gram.

It will be seen that nearly 50 per cent. of the nitrogen was evolved as nitric oxide.

Sodium Nitrite.—Expt. 1. Salt = 0·484 gram.

In the first stage, 7·4 c.c. of nitric oxide and 4·0 c.c. of nitrogen were obtained at 31° and 755 mm., or 8·4 per cent. of the nitrogen in the substance taken. On examining the alkaline liquid, only a trace of absorbed gas was found.

This experiment is of importance in establishing conclusively that in the earlier stages it is nitric oxide more or less mixed with nitrogen that is given off.

Expt. 2. Substance = 0·47 gram.

In the first stage, 27 c.c. of gas ($t = 31°$; $p = 755$ mm.) were collected; a second nitrometer was then employed; after about 2 c.c. more of the gas had been collected, the surface of the mercury lost its lustre and became coated with mercurous nitrate, and the gas assumed a reddish-brown colour, thus proving that oxygen was being eliminated. Once more the nitrometer was changed, this time 9 c.c. of gas were collected, of which 5 c.c. were absorbed by alkaline pyrogallate, the unabsorbed portion being nitrogen.

Magnesium Nitrite.—The stable variety, $Mg(NO_2)_2,2H_2O$, was used, 0·1052 gram being taken. Even at 60°, minute quantities of gas began to be evolved. The decomposition, however, was chiefly effected

* In a recent paper entitled "Uber die Zersetzung des Baryum-nitrates in der Hitze" (*Chem. Zeit.*, 1904, **28**, 356), Gottlieb points out that, when the heating is rapid and not gradual, so as to allow the salt to decompose suddenly before it fuses, the largest amount of nitrous fumes is obtained; but when the temperature is gradually raised, the nitrous fumes, acting on the molten mass, undergo dissociation. Gottlieb's object was the regeneration of nitric acid from the barium nitrate. In our investigation, the temperature was always raised slowly and gradually.

at 120°. A slight evolution of nitrous fumes was distinctly perceptible at the outset.

The temperature was now raised to 172—175° for half an hour, but no more gas was evolved, as was proved by the fact that the "click" of the pump was persistent. The collected gas consisted of 9·2 c.c. of nitric oxide and 1·8 c.c. of nitrogen. The alkali in the worm yielded 2·4 c.c. of nitrogen as nitrite at 31° and 755 mm. pressure. The stable residue on examination was found to be a pure nitrate and gave 0·0166 Mg and 0·10 N, whence the ratio of $Mg : N = \frac{0·0166}{24} : \frac{0·10}{14} = 0·007 : 0·00715 = 1 : 1$. It thus had the composition $2MgO,N_2O_5$ or $MgO,Mg(NO_3)_2$. The simplest reaction yielding this compound would be: $2Mg(NO_2)_2 = MgO + Mg(NO_3)_2 + NO + N$. This, however, would require the nitrogen as nitric oxide to be equal in amount to that in the free state, whereas the quantity of the former is actually $2\frac{1}{2}$ times that of the latter. It would thus appear that by far the larger proportion of the salt decomposed according to the equation: $3Mg(NO_2)_2 = 2MgO + Mg(NO_3)_2 + 4NO$. But neither of these equations serves to account for the formation of a considerable amount of nitrite in the alkali of the worm.

Interpretation of the Results.

It will be seen that, in the first stage, when the heating is slow and cautious, nitric oxide is the main gaseous product of decomposition, and that a portion of the salt is converted into nitrate; whilst in the second stage it is nitrate which undergoes decomposition, giving off oxygen. As a matter of fact, several reactions go on side by side, some of which, again, probably overlap, so that no sharp line of demarcation can be laid down between them. Taking barium nitrite as the type, we have the following reactions:

Initial.

$3Ba(NO_2)_2 = 2BaO + Ba(NO_3)_2 + 4NO$ 1

$2Ba(NO_2)_2 = BaO + Ba(NO_3)_2 + NO + N$ 2

Final.

$Ba(NO_3)_2 = BaO + 2NO_2 + O$ 3

whilst intermediate between these we have also,

$Ba(NO_3)_2 = Ba(NO_2)_2 + O_2$ 4

In the earlier stages, it is the nitric oxide and nitrogen, with only traces of oxygen, that pass on through the worm, the oxygen and a

corresponding portion of nitric oxide being absorbed by the caustic potash in the form of nitrite, thus : $2KOH + 2NO + O = 2KNO_2 + H_2O$.

Later on, as a much larger proportion of oxygen begins to be evolved, a mixture of nitrate and nitrite is formed in the glass worm. In the final stage, owing to increased heat, the evolution of oxygen begins to preponderate, and this time it is all the nitric oxide with only its equivalent of oxygen, together with the nitric peroxide, which is absorbed by caustic potash to form varying quantities of nitrate and nitrite. Thus it is oxygen which is collected in the reservoir of the mercury pump.

As the salts were heated in glass tubing, the results might have been slightly vitiated, owing to secondary reactions due to the corrosion of the glass, but in the experiments with calcium and magnesium nitrites the glass was not in the least attacked, and, in this case, the results are in perfect harmony with those obtained from barium and sodium nitrites. It will also be noticed that calcium and magnesium nitrites yielded very little free nitrogen, whereas the barium and sodium salts gave considerable amounts.

It may here also be suggested as a working hypothesis that, as a result of the purely thermal decomposition, a portion of the salts breaks up into the peroxide and nitric oxide, but as the former is unstable, especially under diminished pressure at the temperature at which the scission takes place, it parts with its oxygen both to the nitric oxide and also to the remaining portion of the undecomposed salt in a state of fusion, and that it is in this way that the internal oxidation and reduction are brought about. It may be urged in support of this view that sodium peroxide absorbs nitric oxide forming the nitrite.

Moreover, this kind of self-oxidation and reduction also goes on when an alkali nitrite is heated just above the fusion point in an open crucible and kept in that state for a minute or two; bubbles of nitric oxide are given off and a considerable portion of the nitrite is changed into nitrate.

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XXII.—*The Addition of Sodium Hydrogen Sulphite to Ketonic Compounds.*

By Alfred Walter Stewart, B.Sc., 1851 Exhibition Scholar of the University of Glasgow.

Beilstein, in his *Handbuch* (3rd Edition, vol. I., 999), states that pinacoline forms no additive product with sodium hydrogen sulphite. This statement, together with the current idea that bisulphite compounds are formed only with those ketones which contain an acetyl group, suggested that the hindrance to the formation of a pinacoline bisulphite compound was of a stereochemical character, analogous to that detected by Victor Meyer in his work on the rates of esterification of the aromatic acids. In the literature of the bisulphite compounds, the only reference found was a paper by Angeli (*Atti R. Accad. Lincei*, 1896, **5**, 84), in which he suggested that steric hindrance played a part in the reactions involving the addition of metallic hydrogen sulphites, hydrocyanic acid, and ammonia to carbonyl groups. Angeli appears to have contented himself with this theoretical observation, at least so far as the bisulphite compounds are concerned; and apparently no attempt has been made up to the present to treat the matter by a quantitative method.

The following research was carried out in order to estimate the relative amounts of bisulphite compound formed with different ketones and with a view to ascertaining the hindering effect produced by various groups.

Although no work had been done on the ketonic bisulphite compounds, Ripper (*Monatsh.*, 1900, **21**, 1079) had devised a method for the estimation of aldehydes which depended on the formation of a bisulphite additive product. He found that as the SO_3Na group in the bisulphite compound was not oxidised by iodine solution; the amount formed could be estimated from the difference between the titration values of two solutions: one of pure sodium hydrogen sulphite, the other containing this salt and the aldehyde.

The great difficulty encountered in this method arises from the presence in the solution of hydriodic acid generated by the reaction. This acid, if left free, tends to break up the bisulphite compound, and thus gives an uncertain end-point.

With a view to avoiding this, several other solutions were prepared, among which three only need be mentioned. First, $N/20$ caustic soda was used to titrate the sodium hydrogen sulphite, but the final slight excess of the alkali present decomposed the double compound even more rapidly than the hydriodic acid had done. The other two solutions

were the result of an attempt to make the reaction follow the lines of the equations :

$$NaHSO_3 + 3NaHCO_3 + I_2 = Na_2SO_4 + 2NaI + 2H_2O + 3CO_2 ;$$
$$NaHSO_3 + 2NaHCO_3 + I_2 = NaHSO_4 + 2NaI + H_2O + 2CO_2.$$

Iodine and sodium hydrogen carbonate were made up in a solution of the strength required by each equation, in the hope that, the free hydriodic acid being eliminated as soon as it was formed, the end-point would be unaffected. The results, however, were useless.

There being no other method available, a return was made to the titration with iodine solution. At first, alcoholic solutions of the ketones were used, but finally it was found best to make up an $N/10$ aqueous solution of the ketone, and then dilute to $N/12$ with alcohol. This mixture dissolved most of the common ketones, methyl hexyl ketone and acetophenone only being excluded.

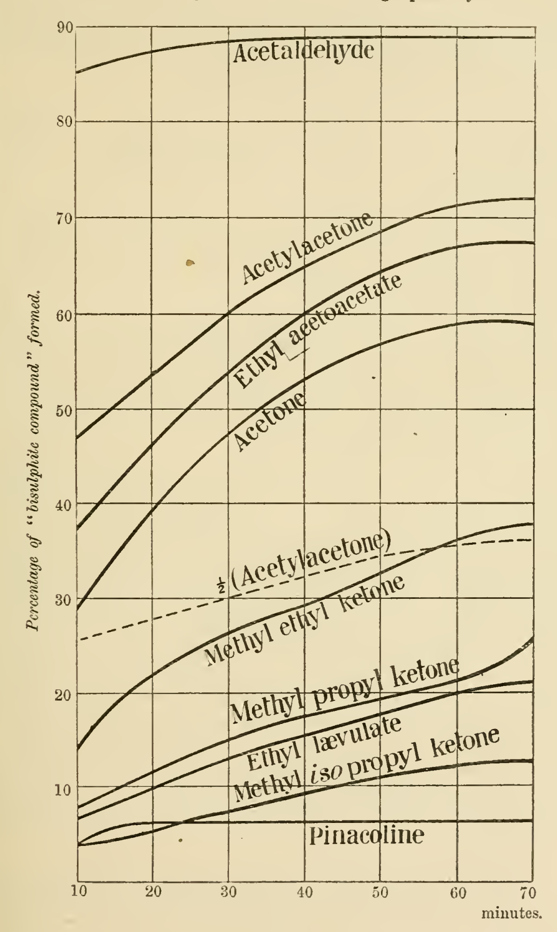
The results were apparently accurate to within one per cent. after allowing equal quantities of ketone and $N/12$ hydrogen sulphite solution to remain together for an hour at the ordinary temperature.

It did not seem desirable to choose an arbitrary time limit, and in the end titrations were done at regular intervals; a period of five minutes was first chosen, but this was not found so satisfactory as the ten-minute interval which was finally adopted. At first the method did not give concordant results, but the failure was traced to variations of temperature. After this, all operations were carried out at 0°, which kept the temperature constant, and also reduced the speed of the reaction.

The details of the method finally adopted were as follows: 50 c.c. of $N/12$ ketone solution, prepared as described, were shaken in a flask with 50 c.c. of $N/12$ aqueous sodium hydrogen sulphite, and then allowed to remain, corked, in a vessel of ice and water. Every ten minutes, 10 c.c. of the liquid were taken out and titrated, being kept surrounded by ice-water during the operation. The iodine solution used was of such a strength that 14—15 c.c. were required to oxidise 5 c.c. of the hydrogen sulphite solution. The relative strengths of the two solutions were determined at the beginning and end of each series of titrations. The results obtained are shown in the following table :

	Percentage of bisulphite compound formed in						
	10	20	30	40	50	60	70 minutes.
Acetaldehyde	85·2	86·6	88·0	88·7	88·7	88·7	88·7
Acetylacetone	47·1	54·2	60 5	64·0	67·6	70·0	71·8
Ethyl acetoacetate	37·4	47·0	56·0	60·0	64·0	67·6	67·6
Acetone.........................	28·5	39·7	47·0	53·6	55·9	56·2	58·9
Methyl ethyl ketone	14·5	22·5	25·1	29·1	32·4	36·4	38·4
Methyl propyl ketone......	8·5	11·0	14·8	18·4	19·6	23·4	25·5
Ethyl lævulate................	7·2	10·0	14·0	15·0	16·5	19·4	21·6
Methyl *iso*propyl ketone .	4·2	5·4	7·5	9·4	11·6	12·3	13·0
Pinacoline	4·2	5·6	5·6	5·6	5·6	5·6	5·6

The following curves give the same results graphically.



Acetylacetone contains two carbonyl groups, therefore the amount of bisulphite compound formed by each group is half the amount shown in the table. This is represented in the curves by the dotted line.

From an examination of the foregoing numbers, the effect of replacing a hydrogen atom by a methyl group is easily seen. If we consider acetaldehyde, acetone, methyl ethyl ketone, methyl *iso*propyl ketone, and pinacoline, and take the percentage of bisulphite compound formed after 40 minutes, we find the following result:

	Per cent.		Per cent.
$CH_3CO{\cdot}H$	88·7	$CH_3CO{\cdot}CH(CH_3)_2$ ...	9·4
$CH_3CO{\cdot}CH_3$	53·6	$CH_3CO{\cdot}C(CH_3)_3$	5·6
$CH_3CO{\cdot}CH_2{\cdot}CH_3$	29·1		

Another point of interest is that both acetaldehyde and pinacoline appear to reach their end-points within the first 40 minutes, whilst the other compounds, intermediate on the scale, do not reach their equilibrium until after 70 minutes.

A curious result is obtained by comparing the values of those compounds containing carbon chains of the same length. For example, ethyl acetoacetate and methyl ethyl ketone each contain a chain of four carbon atoms; ethyl lævulate and methyl propyl ketone have a chain of five. Taking, as before, the percentage of bisulphite compound formed after 40 minutes, we get:

	Per cent.		Per cent.
Ethyl acetoacetate ...	60·0	Methyl propyl ketone.	18·4
Methyl ethyl ketone ..	29·1	Ethyl lævulate	15·0

The carboxyl group seems to have no hindering effect, but rather accelerates the action, since ethyl acetoacetate forms more bisulphite compound than acetone, and much more than methyl ethyl ketone where the CO_2Et group is replaced by methyl. This relation does not hold good in the case of ethyl lævulate, for in this case, when compared with methyl propyl ketone, the ester forms less of the double compound. It seems as if the carbonyl and carboxyl groups had some action on each other's properties when near to one another, and that this is weakened when two carbon atoms are placed between them.

This communication has been limited to those compounds which contain the group $CH_3{\cdot}COR$, but the investigation will subsequently be extended to other ketonic and nitrogen compounds, both with open and closed chains.

In conclusion, the author desires to thank Professor Collie and Dr. Smiles for valuable suggestions made by them during the course of this research.

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XXIII.—*The Molecular Condition in Solution of Ferrous Oxalate.*

By SAMUEL EDWARD SHEPPARD and CHARLES EDWARD KENNETH MEES.

THE investigation of the development of silver haloid emulsions by means of ferrous oxalate makes a knowledge of its condition in solution very desirable. Ferrous oxalate itself is only slightly soluble in water, and the developing solution is prepared by dissolving it in potassium oxalate. This solution has a reddish-brown colour and powerful reducing properties (Eder, *Monatsh.*, 1880, **1**, 137). On treatment with alcohol, a double salt is precipitated having the composition $K_2Fe(C_2O_4)_2,2H_2O$. The precipitate sometimes appears as a red oil, which subsequently crystallises, but more frequently it is obtained as a sludge. This substance is extremely soluble in water, but rapidly decomposes even in a dry state.

If aqueous potassium oxalate is added to the requisite amount of ferrous oxalate to form the double salt, the whole of the ferrous oxalate does not go into solution; further, if equimolecular solutions of ferrous sulphate and potassium oxalate are mixed, ferrous oxalate is precipitated. In general, more of the alkaline oxalate is employed than the proportion required to yield the double salt. Hence, an equilibrium must be established in solution between the amounts of iron and oxalate. The iron is not present to any great extent as free ferrous ions, as the blue precipitate with ferricyanide is only slowly formed. It seems to exist chiefly as the complex anion, $Fe(C_2O_4)_2$ (Rieger, *Zeit. Elektrochem.*, 1901, **7**, 871), to which the colour of the solution is due.

The double salt, therefore, dissociates into $2\overset{+}{K}$ and $\overset{--}{Fe(C_2O_4)_2}$, and the foregoing equilibrium will be of the form

$$\overset{--}{Fe(C_2O_4)_2} \rightleftharpoons \overset{--}{C_2O_4} + FeC_2O_4.$$

In the presence of solid ferrous oxalate, the active mass of the latter will be constant, and we shall have as equilibrium equation:

$$KC_1 = K'C_2, \text{ or}$$
$$C_1/C_2 = K'/K = K, \text{ a constant,}$$

that is, the amount of ferro-oxalanion * in solution bears a constant ratio to the amount of free oxalanion.

To confirm this view and to ascertain the value of the equilibrium

* The ionic terminology employed is that indicated in the English translation of Ostwald's *Anorganische Chemie.*

constant, the solubility of ferrous oxalate in potassium oxalate was determined, the ferrous oxalate being kept in excess; 10 c.c. of a solution containing the molecular weight in grams per litre of potassium oxalate were added, and the whole stirred continuously in a thermostat at 20°.* The potassium oxalate was titrated against $N/10$ potassium permanganate, a similar estimation being subsequently made with the ferrous oxalate mixture. The increase in the titre gave the amount of ferrous oxalate dissolved. Thus, in one estimation, the titrations before and after the addition of ferrous oxalate were respectively 197·8 c.c. and 266·2 c.c. of permanganate. The increase is 68·4 c.c., and the value of

$$K = \frac{C_{Fe(C_2O_4)_2}}{C_{C_2O_4}} \text{ is } \frac{102{\cdot}6}{163{\cdot}6} = 0{\cdot}63.$$

An increase in the time of stirring raised this value to a certain point and then lowered it again. This result is due to saturation only being reached slowly, and then oxidation causing a diminution. The maximum mean value found for

$$K = \frac{C_{FeOx}}{C_{Ox}} \text{ was } 0{\cdot}80\ (\mp 0{\cdot}0{\cdot}2\ \Delta).$$

This result was checked by obtaining the equilibrium from the opposite side. Excess of ferrous sulphate in molecular solution was added to potassium oxalate, and, when ferrous oxalate was no longer precipitated, the solution was titrated. The errors in this case are in the opposite direction, as supersaturation will give too high values of K, whilst oxidation will diminish this constant.

Thus, to 5 c.c. of $2N$ potassium oxalate, 2·0 c.c. of $2N$ ferrous sulphate were added, and, after standing in the thermostat, the solution was titrated with $N/10$ permanganate, filtering off the ferrous oxalate. The difference gave the amount of this salt precipitated, and the following values of $K = \frac{C_{Fe(C_2O_4)_2}}{C_{C_2O_4}}$ were obtained: 0·84, 0·705, 0·72, 0·68, 1·06, 0·915. The mean gives $K = 0{\cdot}82$. The mean of the first series gave $K = 0{\cdot}80$, whence $K = 0{\cdot}81$ at 20°.

This confirms the view of the equilibrium

$$\overset{--}{Fe(C_2O_4)_2} \rightleftarrows \underset{\text{(solid).}}{FeC_2O_4} + \overset{--}{C_2O_4},$$

but the complex may also dissociate in the following manner:

$$\overset{--}{Fe(C_2O_4)_2} \rightleftarrows \overset{++}{Fe} + 2(\overset{--}{C_2O_4}),$$

* For apparatus used, see Walker and Lumsden (Trans., 1902, 81, 353).

giving free ferrous ions, which may take part in development (Luther, *Chemische Vorgänge in der Photographie*), although, as already stated, their concentration is small. The proportion cannot be determined analytically, but spectrophotometric measurements will give some idea of it, as the ferro-oxalanion is highly coloured, while the free ferrous ion is practically colourless (F. Peters, *Zeit. physikal. Chem.*, 1898, **26**, 192). The change occurring on dilution was measured in the Hüfner spectrophotometer (*Zeit. physikal. Chem.*, 1889, 3, 562). In this, the extinction coefficient E is equal to $-\log_e \cos^2\theta$, where θ is the angle of rotation of the analysing Nicol. For convenience, E is given to base 10. The following measurements were obtained on diluting with water at $\lambda = 5420\ \mu\mu$.

Solution strength.	Angle.	E.	Ratio of $E.\frac{a}{b}$.
a. $N/10$ $FeSO_4$ + sat. $K_2C_2O_4$ to 10 c.c...	63·5°	0·700	2·0
b. + Equal vol. H_2O	47·75	0·342	
a. $N/5$ $FeSO_4$ + sat. $K_2C_2O_4$ to 10 c.c. ...	72·95	1·070	1·84
b. + Equal vol. H_2O	59·2	0·582	—
a. $3N/10$ $FeSO_4$ + sat. $K_2C_2O_4$ to 10 c.c...	81·52	1·662	1·92
b. + Equal vol. H_2O	68·4	0·865	—

The measurements were made in a cell of 10 mm. thickness at 17° approximately.

They show that the concentration of the ferro-oxalanion is proportional to the dilution, so that the equilibrium

$$\overset{--}{Fe(C_2O_4)_2} \rightleftarrows \overset{++}{Fe} + 2\overset{--}{C_2O_4}$$

is practically negligible.

The following measurements exhibit the absorption spectrum at three higher concentrations. The extinction-coefficient E was plotted against wave-length. The coefficients E_a, E_b, E_c in the following table correspond with a concentration of ferrous sulphate in a saturated potassium oxalate solution of $N/10$, $N/5$, and $3N/10$ strength respectively.

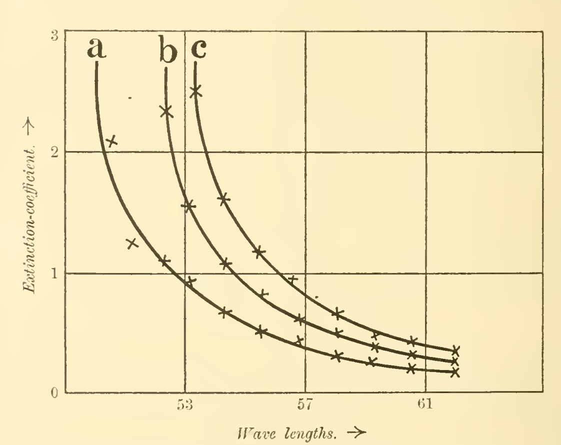
Wave length.	E_a.	E_b.	E_c.	Wave length.	E_a.	E_b.	E_c.
6200	0·144	0·174	0·180	5420	0·700	1·068	1·668
6070	0·153	0·264	0·332	5280	0·852	1·542	2·562
5930	0·184	0·294	0·388	5120	1·142	—	—
5800	0·284	0·366	0·570	5100	1·232	—	—
5670	0·350	0·576	0·892	5020	2·120	—	—
5540	0·504	0·872	1·202	4930	∞	—	—

Influence of Acids.

As all the developing solutions employed were slightly acidified with sulphuric acid, the action of acids is interesting. If increasing quantities of an acid are added to a ferrous oxalate solution, a point is soon reached when ferrous oxalate is precipitated. This must be due to a disturbance of the equilibrium

$$\overset{-\ -}{Fe(C_2O_4)_2} \rightleftarrows FeC_2O_4 + \overset{-\ -}{C_2O_4},$$

and on the ionic theory this is obviously due to the removal of the oxalanion according to the equation: $\overset{-\ -}{C_2O_4} + 2\overset{+}{H} \rightleftarrows H_2C_2O_4$, oxalic



Absorption spectrum of ferrous oxalate in potassium oxalate.

acid, as a "weak" acid, being much less dissociated than its salts. The disturbance therefore increases with the "strength" of the acid, and qualitative tests supported this view. Neglecting any formation of ferrous ions, the equation

$$\frac{C_{Fe(C_2O_4)_2}}{C_{Fe(C_2O_4)}} = KC_{C_2O_4}$$

may be said to measure the complexity ratio (Donnan and Basset, Trans, 1902, **81**, 945) of the ferro-oxalanion, and the measurements show that the complex ion is not very stable, since a considerable excess of free oxalate is required to keep the ferro-oxalanion undis-

sociated. It may be pointed out that solutions supersaturated with respect to ferrous oxalate are easily prepared, and this explains the complete solution of the double salt $K_2Fe(C_2O_4)_2,2H_2O$ when prepared according to Souchay and Lenssen's method (*Annalen*, 1858, **105**, 255). This solution is supersaturated with respect to ferrous oxalate. The molecular condition of ferric oxalate solutions is more complex, as this salt itself is soluble. It is uncertain whether the complex anion has the formula $\overset{-\;-}{\mathrm{Fe}(C_2O_4)_2}$ or $\overset{-\;-\;-}{\mathrm{Fe}(C_2O_4)_3}$; double salts corresponding with both are known, and probably both are existent in ferric oxalate solutions. The ferric complexes are probably more stable than the ferrous, in agreement with Abegg and Bodländer's theory of electro-affinity (*Zeit. anorg. Chem.*, 1899, **20**, 453).

Summary.

(1) The iron is chiefly present as the complex anion $\overset{-\;-}{\mathrm{Fe}(C_2O_4)_2}$; this, however, is not very stable, and for the dissociation

$$\overset{-\;-}{\mathrm{Fe}(C_2O_4)_2} \rightleftharpoons \underset{\text{(solid).}}{\mathrm{FeC_2O_4}} + \overset{-\;-}{\mathrm{C_2O_4}},$$

the equation $\frac{C_{\mathrm{Fe}(C_2O_4)_2}}{C_{C_2O_4}} = K$ holds, the value found for K being 0·81 at 20°.

(2) Spectrophotometric measurements showed that at moderate concentration the dissociation

$$\overset{-\;-}{\mathrm{Fe}(C_2O_4)_2} \rightleftharpoons \overset{++}{\mathrm{Fe}} + 2\overset{-\;-}{\mathrm{C_2O_4}}$$

is negligible.

(3) The action of acids is to precipitate ferrous oxalate by disturbing the equilibrium in (1).

(4) The absorption spectrum at three concentrations is given.

In conclusion, the authors desire to express their thanks to Professor Sir William Ramsay, F.R.S., for his interest in the work.

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XXIV.—*The Determination of Molecular Weight by Lowering of Vapour Pressure.*

By EDGAR PHILIP PERMAN.

MANY attempts have been made to determine the molecular weights of substances by means of the lowering of vapour pressure of the solvent in which the substances are dissolved, but hitherto no simple and satisfactory method has been elaborated, and it is usually stated in text-books on physical chemistry that the method is of no practical value. The object of this paper is to rescue the method from the neglect to which it has been consigned.

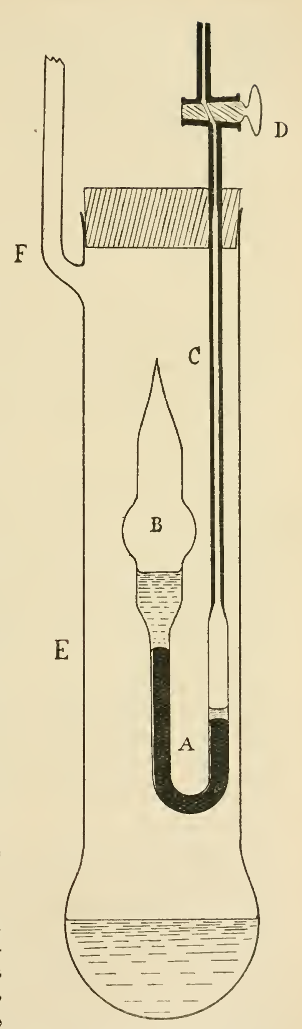
It was proposed by Ostwald (*Grundriss der allgemeinen Chemie*, 1889, p. 134) to heat the solution in the vapour of the pure solvent boiling under atmospheric pressure, and to read off directly the difference between the vapour pressure of the solvent (that is, the atmospheric pressure) and that of the solution. Although this differential method is very simple theoretically, yet practically there are many difficulties to be overcome. I believe I have so far mastered these difficulties as to make the method practicable for ordinary laboratory use.

The chief difficulty is to drive out of the solution every trace of air, and to prevent it from re-entering. In my first experiments, I obtained a normal depression of vapour pressure, which slowly decreased until it became zero. After ascribing this to leaks and to superheating, I discovered the true cause to be a trace of air left in the solution, which is gradually evolved on continued heating. The air can, however, be completely expelled by sufficiently long boiling.

Apparatus.—The apparatus consists of a U-tube, *A*, 4·5 mm. in diameter, connected on one side with a long tube, *C*, about 1·3 mm. in diameter, and on the other side with a short tube, *B*, about 14 mm. in diameter, and having a small bulb blown in the centre. The lengths are approximately as follows: the tube *A*, each limb, 7 cm., the tube *B* 6 cm. (wide portion only), the tube *C* 23 cm. to stopcock *D*, which is of 0·5 mm. bore, and should be "diagonal" and thoroughly well ground.

The dimensions may be varied somewhat, but, after many trials, these have been found to work best. The diameter of *C* must not be much less than that given, especially if water is used as a solvent, for otherwise columns of liquid are formed which make the pressure unreadable. The whole is heated in a vapour jacket, *E*, and is held by a split cork, which, however, need not be completely divided. *F* is a

condenser tube fused on to *E*, but it may pass through the cork, when the apparatus will be somewhat simpler to make.



Method of Experimenting.—In order to ensure success, the details of the manipulation must be very carefully followed. The inner tube is removed from the outer jacket, inverted, and clamped just above the stopcock; it is then exhausted by means of a water-air pump, the connection being made most conveniently with a long piece of thick-walled indiarubber tube. The stopcock is turned, and mercury is admitted in sufficient quantity to serve as a pressure gauge (after one or two trials this will be judged very easily). The mercury is allowed to run into the wide part of the tube, which is then again exhausted and weighed, together with the mercury it contains, to 0·01 gram. The most convenient way of supporting the tube on the balance is to let the bottom of the U rest on the pan, and to maintain the tube in position by a loop of wire, which slides along the narrow tube, *C*, and may be fixed over the hook of the balance.

The next operations are to invert the tube again and to tap out any air-bubbles appearing between the mercury and the glass; there is no difficulty in effecting this, unless the end of the tube *B* is drawn into too fine a point.

The solution is made up in a small weighing bottle, in which the substance under investigation is first weighed, and is then introduced into the tube by carefully turning the stopcock, the weighing bottle being rinsed by two or three small quantities of the solvent.

The tube is left open to the air, and the solution is boiled briskly by a small Bunsen burner flame, the burner being waved gently underneath the wide tube, *B*.

This method of boiling out has been found by careful trial to be the most successful in avoiding bumping, and can be adapted to any solvent. Ether can be boiled out very easily in this way. Chloroform condenses entirely in the narrow tube, unless the latter is also heated, and the boiling is best effected by a large flame moved to and fro along the tube. The solution should be reduced to about half its bulk, and the stopcock is then turned. If there is any liquid in the capillary tube outside the stopcock, it must be removed by the pump. The tube and contents are next weighed again, and the excess over the previous weighing gives the weight of the solution; on deducting from this the weight of the substance taken, the weight of the solvent is obtained.

The tube is now placed in the vapour jacket and heated steadily. If a long column of liquid should remain in the narrow tube, *C*, it is best to withdraw it by means of the pump, turning the stopcock very cautiously.

When the solution has been heated 2 or 3 minutes, the stopcock may be opened, when the mercury will, as a rule, be slowly depressed. Readings should be taken between 5 and 10 minutes after the solution begins to be directly heated in the vapour; the tube should be shaken by tapping, or, better, by rocking the projecting tube slightly. Even if a trace of air remains in the solution, accurate readings can be obtained if made not more than 10 minutes after the heating has begun.

The depression is thus obtained, but it must be corrected for the solution above the mercury column on each side. For this purpose, the heights of the solution are read as well as the mercury, and in order to obtain the relation between the density of the solution and that of the mercury the point of the tube *C* is broken, and readings of both mercury and solution again made under atmospheric pressure on each side.

The length of the left-hand column (see figure) will not be the same at the second reading as at the first, owing to the varying diameter of the tube, but a proportional correction is easily made. The heights can be read conveniently on a mirror scale placed behind the whole apparatus, or the U-tube may be graduated, or, again, a reading microscope may be employed. For the convenience of those using the method, the various operations are here concisely stated: exhaust—introduce mercury—exhaust—weigh. Tap out air-bubbles—introduce solution—boil out—remove any liquid outside stopcock, and weigh.

Heat the apparatus in the vapour jacket—if necessary pump out solution in narrow tube—open to the air—read—turn off stopcock—break off the point of the tube, reopen stopcock and read the data for the correction. It is necessary also to read the barometric height.

Calculation of Results.—Let m be the required molecular weight, M the molecular weight of the solvent, w the weight (in grams) of the substance taken, and W the weight of the solvent, p the height of the barometer, and d the depression; then $m = \frac{w.\ M.\ p.}{W.\ d.}$.

The following results have been obtained:

Substance.	Solvent.	w. grams.	W. grams.	p. mm.	d. mm.	m.	m (calc.).
Carbamide	Water	0·4772	5·43	772·0	20·5	59·6	60
,, ...	,,	0·4594	3·76	772·0	28·5	59·6	60
,, ...	,,	0·3136	5·90	773·6	13·0	56·9	60
,, ...	,,	0·9858	4·82	770·0	42·0	67·5	60
,, ...	,,	1·459	3·93	765·0	65·0	78·6	60
Cane sugar..................	,,	0·9582	2·64	754·8	14·5	340·0	342
,, ...	,,	0·3710	2·65	733·3	5·5	336·0	342
p-Nitrotoluene	Chloroform	0·0726	2·42	770·9	20·0	138·0	137
,, ...	,,	0·0754	2·86	776·7	16·9	144·5	137
Phenyl salicylate	,,	0·1894	2·73	775·4	31·1	206·4	214
2-Phenyl-1:3-dimethyl-1:3-dibenzoylpropane	,,	0·2202	2·79	775·4	21·6	338·0	356
	,,	0·2202	3·25	766·9	16·3	380·0	356
β-Naphthol	,,	0·1056	3·13	772·1	21·9	142·0	144
,, ...	,,	0·1988	4·58	770·2	28·9	138·0	144
Naphthalene	Ether	0·1235	2·29	754·6	23·7	127·0	128
,, ...	,,	0·1512	1·30	754·6	50·5	129·0	128
Diphenylamine	,,	0·1636	1·79	766·8	29·0	179·0	169
,, ...	,,	0·1779	1·39	766·8	40·7	178·0	169
,, ...	,,	0·1642	1·78	760·4	32·9	158·0	169
,, ...	,,	0·1744	1·70	766·8	34·9	167·0	169
				Mean		170·5	

It will be seen that the results are as good as, and often even better than, those usually obtained by the boiling point method. The last two with carbamide in water are from very concentrated solutions, so that the normal molecular weight could not be expected. The aqueous solutions were not heated in exactly the same way as the others, the source of heat being steam blown in from another vessel; the temperature was probably more constant than with the other solvents. The method is well suited for ordinary laboratory use, especially for teaching purposes. The apparatus required is simple and inexpensive.

In conclusion, I wish to express my best thanks to Mr. J. H. Davies, B.Sc., for the valuable assistance he has given me in carrying out the work.

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XXV.—*Electrolytic Oxidation of Aliphatic Aldehydes.*

By HERBERT DRAKE LAW.

ALTHOUGH many investigators have studied the electrolytic oxidation of the acids and alcohols of the aliphatic series, very little is known of the behaviour of the corresponding aldehydes when subjected to the action of electrolytic oxygen. For this reason, it seemed to be of interest to study the action of anodic oxygen on certain aldehydes of the aliphatic series. To a certain extent, the choice of the aldehydes was circumscribed, because those having a higher formula than $C_4H_{10}O$ are practically insoluble in water or dilute acids.

Two sets of experiments have been carried out, the first to ascertain the volatile or gaseous substances which are produced, and the second to study the non-volatile or soluble constituents. The products obtained by the action of the electrolytic current may vary very considerably between the beginning and the end of the electrolysis. That is, the results obtained may be very much complicated by secondary changes, because the substance first produced by the electric current may itself be further affected.

For studying the gaseous products, Hofmann's apparatus, such as is employed for showing the volumetric constitution of water, was used. For studying the soluble products, a porous cell was employed as anode compartment and a beaker placed in a vessel of cold water as cathode compartment. In the experimental portion of this paper, the production of the gaseous substances will be considered first.

EXPERIMENTAL.

Both limbs of a Hofmann's apparatus were graduated, and the junction between the tubes was packed with filter paper to act as a diaphragm and to prevent diffusion of the gaseous products from the anode and cathode. The electrodes were of sheet platinum, the active surface of which was 12·5 square centimetres.

The gases to be analysed were either measured directly in the Hofmann's apparatus or were first run into a graduated pipette. The

Formaldehyde.

Solution.	Current in amperes.	*E.M.F.* in volts.	Time.	Press. in mm. of Hg.	Carbon dioxide in c.c.	Carbon monoxide in c.c.	Oxygen in c.c.	Total vol. of gas.	Temp.
a. 7 grams of formaldehyde, 20 grams of sulphuric acid...... (Total vol. = 200 c.c.)	0·2	4·0	4 h. 5 m.	760	1·6	16·4	30·0	51·0	14°
b. 20 grams of formaldehyde. Solution as before	0·2	5·5	3 h. 5 m.	767	0·8	7·4	7·4	17·2	17
c. Solution as in *b*	0·2	5·5	3 h. 50 m.	767	17·6	14·5	11·0	44·6	17
d. 30 grams of formaldehyde, other conditions as before ...	0·2	6·5	6 h. 10 m.	754	8·0	19·8	11·8	41·0	15
e. Solution as in *d*	0·2	6·5	2 h.	754	4·2	9·5	5·8	21·0	15
f. 20 grams of formaldehyde. Solution as before	0·5	10·5	45 m.	752	0·4	9·6	7·2	19·2	15
g. 20 grams of formaldehyde, 4 grams of sulphuric acid...... (Total vol. = 200 c.c.)	0·2	12—15	4 h. 20 m.	752	4·8	7·2	7·0	21·6	15
h. 20 grams of formaldehyde, 20 grams of sodium hydroxide. (Total vol. = 200 c.c.)	0·2	11·0	14 h.	752	—	6·0	—	—	14

analysis of the gases was conducted by means of Hempel's bulbs. In these experiments, the gases liberated were carbon dioxide, carbon monoxide, oxygen, methane, and ethane. The oxygen was absorbed in an alkaline solution of potassium pyrogallate, and the hydrocarbons were determined by explosion with oxygen. The current used was measured on an ammeter previously graduated against an oxygen coulombmeter. For the non-volatile products, the electrolysis was conducted in a porous pot of about 400 c.c. capacity. This was fitted with a cork, through which passed a rotating platinum anode, the area of which was 37·5 sq. cm. A piece of stout platinum wire wound round the porous pot served as cathode. The anode compartment was placed in a stout glass jar, which in turn was surrounded by another vessel through which cold water could be circulated in order to keep the apparatus cool during the experiment. In these experiments, monobasic acids containing the same number of carbon atoms as the aldehyde were detected. In most cases, sulphuric acid was used to render the solution conductive. The amount of acid formed was determined by first estimating the total acidity of the solution by titration against normal caustic soda. The amount of sulphuric acid present was then found by precipitation with barium chloride, and the difference gave the acidity due to the organic acid.

The experiments indicated in the foregoing table show the effects of varying conditions on the gaseous products of oxidation. In experiment *c*, the solution from *b* was allowed to run back from the reservoir and was electrolysed again to determine the influence of the accumulated formic acid. This also applies to experiment *e*, which is a repetition of *d*. Experiments *f*, *g*, *h* show the effects produced by changing the constitution of the electrolyte. In *h*, only the carbon monoxide was estimated, as the carbon dioxide was absorbed in the sodium hydroxide present as electrolyte. To compare the results, the following table is given:

I.

Strength of aldehyde.	Ampere hours.	Oxygen equivalent to 2 ampere hours.	Vol. of gas.	Carbon dioxide.	Oxygen.	Carbon monoxide.
1. 3·5 per cent...	2	417 c.c.	124·9 c.c.	3·9 c.c.	73·5 c.c.	40·2 c.c.
2. 10 ,, ...	2	417 ,,	55·8 ,,	2·6 ,,	24·0 ,,	24·0 ,,
3. 10 ,, ...	2	417 ,,	88·3 ,,	26·3 ,,	26·3 ,,	31·3 ,,
4. 15 ,, ...	2	417 ,,	66·5 ,,	12·9 ,,	19·2 ,,	32·1 ,,
5. 15 ,, ...	2	417 ,,	75·9 ,,	14·9 ,,	23·6 ,,	35·9 ,,
6. 10 ,, ... (high *E.M.F.*)	2	417 ,,	102·4 ,,	2·1 ,,	38·4 ,,	51·2 ,,
7. 10 per cent... (dilute acid).	2	417 ,,	49·8 ,,	11·1 ,,	16·2 ,,	16·6 ,,
8. 10 per cent.. (sodium hydroxide).	2	417 ,,	—	—	12·9 ,,	4·3 ,,

In all the preceding experiments, and in those which follow, the

results varied somewhat on repetition, and for this reason the mean of two or more experiments is given. In the above table, experiment 2 corresponds with *b*, previously given. Here only a small volume of gas was liberated, and therefore a mean value of experiments *b* and *c* is given in 3 for comparison. Number 5 is also the mean of experiments *d* and *e*. Numbers 6, 7, and 8 correspond with *f*, *h*, and *g*. Numbers 1 to 5 show the effects of a change in the concentration of the formaldehyde.

The formation of carbon monoxide may be represented as in equation V. From this it would be expected that changes in the concentration of the aldehyde would have very little effect on the quantity of this gas formed. The amount of oxygen set free of course decreases as the concentration increases. In number 7, with more dilute acid, the amount of active oxygen set free should be increased, and consequently the amount of carbon monoxide liberated should increase. However, the *E.M.F.* was much higher in this experiment, and so the tendency to form carbon dioxide directly from the aldehyde will be greater, as is actually the case.

In experiment 8, where sodium hydroxide is used as electrolyte, the hydroxide group will be liberated at the anode, and active oxygen will be formed only as the result of a secondary reaction. Consequently, the amount of carbon monoxide formed from this oxygen will be smaller than in the other experiments. The formation of this gas favours the assumption of quadrivalent oxygen.

Non-volatile Portions.

These were found to be formic acid, the formation of which may be represented as in equation I (p. 203).

Solution.	Current in amperes.	*E.M.F.* in volts.	Ampere hours.	Acid calculated in c.c. of oxygen.	Total oxygen liberated in c.c.
i. 20 grams of formaldehyde, 37 grams of sulphuric acid (Total vol. = 370 c.c.)	2·0	3—4	10	1423	2085
ii. 30 grams of formaldehyde, conditions as before ……	4·0	7·0	10	1550	2085
iii. 30 grams of formaldehyde, conditions as before ……	2·0	3—4	10	1579	2085

In these experiments, the cathode solution consisted of 10 per cent. sulphuric acid; the acid formed is given in terms of the oxygen required to produce this quantity of acid. These results agree with the preceding ones. If the total yield of oxygen is calculated from experiment iii and experiment 6 of Table I, the result is 0·7 per cent. too high, thus the agreement is fairly good.

Acetaldehyde.

Solution.	Current in amperes.	Time.	*E.M.F.* in volts.	Temp.	Pressure in mm.	Carbon dioxide in c.c.	Carbon monoxide in c.c.	Oxygen in c.c.	Methane in c.c.	Total vol. in c.c.
a. 8 grams of acetaldehyde, 20 grams of sulphuric acid. (Total vol. = 200 c.c.)	0·2	6 h. 45 m.	4·0	15°	760	0·8	0·2	18·8	1·0	23·0
b. 20 grams of acetaldehyde, conditions as in *a*.........	0·2	36 h. 30 m.	5·0	18	749	28·8	2·0	19·6	5·6	58·0
c. 30 grams of acetaldehyde, conditions as in *a*.........	0·2	26 h. 20 m.	5·5	16	757	37·8	1·0	3·4	5·6	51·0
d. 20 grams of acetaldehyde, conditions as in *a*.........	0·4	15 h. 45 m.	8·5—9	17	750	23·0	1·6	17·0	3·4	47·0
e. Solution as in *d*..............	0·6	7 h. 40 m.	9—9·5	14	755	35·2	3·0	28·4	3·6	72·6

Propaldehyde.

Solution.	Current in amperes.	*E.M.F.* in volts.	Time.	Temp.	Pressure in mm.	Carbon dioxide in c.c.	Carbon monoxide in c.c.	Oxygen in c.c.	Ethane in c.c.	Total vol. in c.c.
a. 8 grams of propaldehyde, 20 grams of sulphuric acid. (Total vol. = 200 c.c.)	0·1	3·5	22 h. 5 m.	16°	754	36·8	25·4	24·2	4·4	95·0
b. Solution as in *a*..............	0·2	5·0	11 h. 50 m.	17	754	24·0	17·4	62·5	3·4	110·8

III.

Strength of aldehyde.	Ampere hours.	Oxygen equivalent to 2 ampere hours.	Volume of gas in c.c.	Carbon dioxide in c.c.	Carbon monoxide in c.c.	Oxygen in c.c.	Ethane in c.c.
1. 4 per cent.	2	417	86·0	33·3	23·0	21·9	4·0
2. 4 per cent. .... (Higher *E.M.F.*)	2	417	93·6	20·3	14·7	52·8	2·9

In experiments *a*, *b*, *c*, the effects of a change in concentration of the aldehyde are shown. In *d* and *e*, the current density has been changed. To compare these results, the following table is given. Here it will be seen that the absorption of oxygen is very complete, the bulk being used to form acetic acid.

II.

Strength of aldehyde.	Ampere hours.	Vol. of gas in c.c.	Carbon dioxide in c.c.	Carbon monoxide in c.c.	Oxygen in c.c.	Methane in c.c.	Oxygen equivalent in 2 ampere hours.
1. 4 per cent...	2	34·0	1·1	0·3	28·0	1·4	417
2. 10 ,, ...	2	15·9	7·9	0·5	5·4	1·5	417
3. 15 ,, ...	2	19·3	14·4	0·4	1·3	2·1	417
4. 10 ,, ... (current = 0·4).	2	18·4	9·0	0·6	7·3	1·3	417
5. 10 per cent... (current = 0·6).	2	31·6	15·5	1·3	12·4	1·5	417

The following equations represent the formation of each product :

I. $RC{<}^{O}_{H} \quad -OH \quad -OH \quad = \quad RC{<}^{O}_{OH} + H_2O.$

II. $HO- \quad R-C{<}^{O}_{OH} \quad -OH \quad = \quad ROH + CO_2 + H_2O.$

III. $^{R}_{H}{>}C{:}O \quad O \quad = \quad RH + CO_2.$

IV. $O \quad ^{R}_{H}{>}C{:}O \quad O \quad = \quad ROH + CO_2.$

V. $O \quad ^{R}_{H}{>}C{:}O \quad = \quad ROH + CO.$

As in the previous set of experiments, the carbon dioxide increases as the oxidation proceeds. Thus, it must be assumed that part of this gas is formed by the further oxidation of the acetic acid accumulated during the electrolysis. Carbon dioxide, however, is always present in the gases at the anode. For this reason, equations III and IV are given. Equation III also indicates the formation of methane and ethane. Equation V shows the formation of carbon monoxide. According to these equations, alcohol should be formed. However, the quantity of this substance must have been very small and in no case could it be detected. According to equation III, the amount of carbon dioxide present should never be less than that of the hydrocarbon. Number 1, Table II, however, shows a slightly smaller proportion ;

this was found to be due to the fact that the anode solution was not quite saturated with carbon dioxide on commencing, and as the experiment proceeded results were obtained agreeing with the theory. On exploding the methane with oxygen, a decrease in volume should take place. On absorbing the carbon dioxide formed, there should be a further decrease, and these two diminutions should be in the ratio of 2 : 1. The mean ratio for four different explosions was found to be 31·8 : 16. This agrees with the theoretical value. The gas was inflammable, but the quantity was so small that no further experiments could be undertaken.

Non-volatile Portions.

In these experiments, nothing but acetic acid was detected.

Solution.	Current in amperes.	*E.M.F.* in volts.	Ampere hours.	Acid calculated in c.c. of oxygen.	Total oxygen liberated in c.c.
i. 15 grams of acetaldehyde, 37 grams of sulphuric acid (Total vol. = 370 c.c.)	2·0	4—4·5	11·5	2099	2398
ii. 30 grams of acetaldehyde, conditions as before.........	5·0	7·0	12·9	2368	2690

The cathode solution consisted of 10 per cent. sulphuric acid; the amount of acid formed is given in terms of the oxygen required to produce this change. The calculation of the total yield of oxygen in experiments ii and 5 (Table II) gives a result 3 per cent. too high. Considering that the conditions were not quite the same, the agreement is good.

The gases liberated in the above experiments were shaken up with fuming sulphuric acid. A small diminution in volume occurred, but this never amounted to more than 0·2 c.c. It was concluded therefore that no unsaturated hydrocarbons were present in the gaseous mixture. The equations already given hold good in this case, *R* now representing the ethyl group, as before the residual gases were analysed by explosion. The ratio of the two diminutions in volume was found to be 13 : 10·1 in three experiments, whilst the theory requires a ratio of 13 : 10·4. This gas was inflammable, but no further experiments were conducted, as the volume was very small.

Non-volatile Portions.

Solution.	Current in amperes.	*E.M.F.* in volts.	Ampere hours.	Acid in terms of oxygen.	Total oxygen liberated in c.c.
14 grams of propaldehyde 35 grams of sulphuric acid. (Total vol. = 350 c.c.)	2·0	3·5	10	1540	2085

In this experiment, the cathode solution was 10 per cent. sulphuric acid. The total oxygen used in this experiment and 2 (Table III) gives a result 1·7 per cent. higher than that required by theory.

iso*Butaldehyde.*

Solution.	Temp.	Current in amperes.	*E.M.F.* in volts.	Time.	Press. in mm.	Carbon dioxide in c.c.	Carbon monoxide in c.c.	Oxygen in c.c.	Total vol. in c.c.
4 grams of *iso*-butaldehyde, 20 grams of sulphuric acid (Total vol. = 200 c.c.)	16°	0·2	4	1 h. 20 m.	756	4·2	0·0	44·2	49·6

IV.

Strength of solution.	Ampere hours.	Oxygen equivalent to 2 ampere hours.	Vol. of gas in c.c.	Carbon monoxide in c.c.	Carbon dioxide in c.c.	Oxygen in c.c.
2 per cent.	2	417	369·5	31·5	0·0	331·5

In this case, the aldehyde is only slightly soluble in water. This may account for the absence of carbon monoxide and the hydrocarbons.

Non-volatile Portions.

Solution.	Current in amperes.	*E.M.F.* in volts.	Ampere hours.	Acid calculated in c.c. of oxygen.	Total oxygen liberated.
2 per cent. solution of *iso*butaldehyde, 37 grams of sulphuric acid... .... (Total vol. = 370 c.c.)	2·0	2·5	10	177	2085

The cathode cell contained 10 per cent. sulphuric acid. A calculation of the amount of oxygen used in the two preceding experiments gives a result 3·5 per cent. too high. The agreement with the theory is good, considering that the amount of oxygen absorbed is very small.

Conclusions.

Starting from an alcohol, the oxidation takes place in the following stages :

$$\begin{array}{ccccc} RCH_2{\cdot}OH & \rightarrow & RCH{:}O & \rightarrow & RCO{\cdot}OH \\ \downarrow & & & & \downarrow \\ R{\cdot}CO{\cdot}OH & & \longrightarrow & & C{<}^{O}_{O} \end{array}$$

In addition to these products, smaller quantities of other substances are formed, but the chief reactions are as indicated on p. 203. In this work, the formation of alcohols has been assumed in equations II, IV, and V, but the quantity of these substances produced would,

however, be too small to be detected. They are formed, however, during the oxidation of the aliphatic acids represented in equation II (Kolbe, Hofer, and Moest, *Annalen*, 1902, 323, 304; Foerster and Piguet, *Zeit. Elektrochem.*, 1904, 10, 729). From this point, the oxidation would go on as in the foregoing scheme. Thus, it is possible that in the oxidation of the compounds of the aliphatic series there is a gradual breaking up into compounds containing less and less carbon atoms until the final stage—carbon dioxide—is reached. One step in the oxidation is still missing. So far, the hydrocarbons have given no oxidation products. Numerous attempts which have been made in this laboratory to bring about this step have led to a method which promises to be successful. On oxidising the alkyl iodides, a precipitation of iodine is obtained, and the corresponding acid is found in solution, $RCH_2I \longrightarrow RC{<}^{O}_{I} \longrightarrow RC{<}^{O}_{OH} + HI$, the hydriodic acid supplying the liberated iodine. This behaviour would agree with that of the aromatic hydrocarbons (Law and Perkin, *Trans. Faraday Soc.*, 1905, I, 31).

If these views are correct, during the oxidation of acetic acid a small quantity of formic acid will be produced, and it was thought that the formation of this substance might account for the appearance of the hydrocarbons in the following manner:

$$\begin{matrix} H\,C{<}^{O}_{O-} \\ CH_3\,C{<}^{O}_{O-} \end{matrix} \longrightarrow CH_4 + 2CO_2.$$

This has been tried, but without success. Further experiments with these aldehydes are still in progress.

In conclusion, I wish to express my gratitude to Dr. F. Mollwo Perkin for the facilities and help given during this work.

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XXVI.—*The Analysis of Samples of Milk referred to the Government Laboratory in connection with the Sale of Food and Drugs Acts.*

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In connection with the administration of the Sale of Food and Drugs Acts, samples of milk are frequently referred by magistrates,

under the provisions of the Acts, to the Government Laboratory for examination.

These referred samples are invariably more or less sour when received, and hence it is of importance to determine whether this fact in any way prevents a true inference as to the character of the fresh milk, or interferes with the determination of the degree of sophistication to which the milk may have been subjected.

The charges usually brought against milk by public analysts are that it has been mixed with water, or with skim-milk. The proof or disproof of the allegation depends upon a determination in the sample (1) of the amount of fat; and (2) of the total amount of the constituents other than fat and water.

As regards the fat, it would appear that bacteria which produce steatolytic enzymes do not develop to any considerable extent in sour milk. At all events, the amount of butter-fat suffers little, if any, alteration during the souring of the milk. Experimental proof of this is afforded by the following figures:

Sample.		Fat, per cent.
No. 1.	Fresh milk	4·08
	After 12 weeks	4·09
No. 2.	Fresh milk	3·17
	After 4 weeks	3·16
No. 3.	Fresh milk	4·16
	After 6 weeks	4·18
	,, 14½ ,,	4·18
No. 4.	Fresh milk	4·72
	After 6 weeks	4·65
No. 5.	Fresh milk	3·28
	After 7½ weeks	3·25
	,, 11 ,,	3·34
	,, 13 ,,	3·27
No. 6.	Fresh milk	4·49
	After 8 weeks	4·35
No. 7.	Fresh milk	4·07
	After 11 weeks	4·06

Sample.		Fat, per cent.
No. 8.	Fresh milk	4·19
	After 13 weeks	4·14
No. 9.	Fresh milk	4·07
	After 13 weeks	4·01
No. 10.	Fresh milk	3·70
	After 13 weeks	3·69
No. 11.	Fresh milk	5·32
	After 13 weeks	5·20
No. 12.	Fresh milk	3·98
	After 13 weeks	3·83
No. 13.	Fresh milk	3·58
	After 2 weeks	3·57
	,, 4 ,,	3·53
	,, 6 ,,	3·53
	,, 8 ,,	3·51

The results are not affected by the presence of added water. Thus, by the addition of 10 per cent. of water:—

Sample.		Fat, per cent.
No. 1.	Fresh milk	3·44
	After 2 weeks	3·41
	,, 4 ,,	3·40

Sample.		Fat, per cent.
No. 2.	Fresh milk	2·79
	After 5½ weeks	2·78 / 2·76

With approximately 25 per cent. of added water:

Sample.	Fat, per cent.	Sample.	Fat, per cent.
No. 1. Fresh milk	2·84	No. 2. Fresh milk	1·72
After 2 weeks	2·89	After 2 weeks	1·71
,, 4 ,,	2·84	,, 4 ,,	1·73
,, 6 ,,	2·84	,, 6 ,,	1·69
,, 8 ,,	2·85		

These results, it should be noted, were obtained from a great variety of samples in various stages of fermentative change, by assistants working independently, and at different periods during the last ten years, but all using substantially the same method of extraction, both with the fresh and sour milk. The numbers are almost invariably the mean of duplicate experiments which, as a rule, differed among themselves by amounts not greater than 0·02 per cent.

They serve to establish that if the fat in milk suffers any alteration in amount as the milk becomes sour, it is too inconsiderable to affect to any substantial extent the experimental proof of the validity of any charge based on an alleged deficiency in fat.

As regards a charge based on an alleged deficiency of non-fatty solids, the matter is not so simple, for here there is no question that the aggregate weight of the non-fatty solids in milk is affected to a greater or less extent by the fermentative changes associated with its souring. It is necessary, therefore, to examine these changes in some degree of detail, in order to ascertain their bearing on the experimental facts needed to establish the inference of sophistication, and to determine its extent.

As is well known, the principal constituent of milk which suffers change in the process of souring is the lactose. From it lactic acid is formed at an early stage, the rapidity of formation depending, within certain limits, on the temperature. That the production of lactic acid is due to the action of micro-organisms was clearly established by Pasteur, who was the first to describe a characteristic organism of lactic fermentation. Lister in 1877, Hueppe in 1884, and Günther and Thierfelder in 1894, amongst other observers, have isolated and described various bacteria capable of transforming lactose into lactic acid, and it has been stated that upwards of 100 kinds of micro-organisms are now known to have the power of effecting this change (Swithinbank and Newman, *Bacteriology of Milk*, p. 156).

The chemical transformation of lactose into lactic acid is usually expressed as follows:

$$\underset{\alpha\text{-Lactose.}}{C_{12}H_{22}O_{11},H_2O} = \underset{d\text{-Glucose.}}{C_6H_{12}O_6} + \underset{d\text{-Galactose.}}{C_6H_{12}O_6}$$

$$\underset{d\text{-Galactose.}}{C_6H_{12}O_6} = \underset{(d+l)\text{ Lactic acid.}}{2CH_3{\cdot}CH(OH){\cdot}CO_2H}$$

It will be observed that no loss of weight is involved in the change as thus represented.

It is further known that only a portion of the lactose is transformed into lactic acid in the souring of milk under ordinary conditions. When the lactic acid reaches a certain amount, the activity of the micro-organisms concerned in the change would appear to be inhibited.

In eight series of experiments made on different milks kept at a mean temperature of about 18° in closed bottles, the amount of non-volatile acid present at the end of a fortnight ranged from 0·65 to 0·91 per cent., calculated as lactic acid. It then slowly increased, reaching a maximum of 1·48 per cent. in one case, at the end of eight weeks. The numbers were as follows:

Non-volatile acid, calculated as lactic acid.

	No. 1.	2.	3.	4.	5.	6.	7.	8.	
At end of 2 weeks......	0·81	0·81	0·91	0·75	0·65	0·68	0·74	0·74	per cent.
,, 4 ,, ...	0·91	0·99	0·89	0·88	0·76	0·90	0·85	0·68	,,
,, 6 ,, ...	0·93	1·28	0·80	0·77	0·85	1·08	0·94	0·65	,,
,, 8 ,, ...	1·17	1·13	1·48	0·86	1·03	1·13	0·54	0·86	,,

Taking the average amount of lactose in milk as 4·75 per cent. and assuming that the maximum figure in the above table—1·48 per cent.—represents lactic acid, and that no lactic acid has been lost by subsequent fermentative change, it would appear that at the end of eight weeks about 62 per cent. of the lactose present has been transformed into lactic acid and dextrose. This is probably an exceptional instance; in the greater number of cases considerably less than half the lactose is transformed.

As already stated, the equations above given, representing the transformation of lactose into lactic acid, show that the change is accompanied by no loss of weight in the amount of the non-fatty solids. Inasmuch as the lactic acid is neutralised in the course of the analysis by a known weight of strontia and weighed with the other milk solids, the total weight, less the corresponding weight of strontia, should be equivalent to the weight of the non-fatty solids in the fresh milk, provided no other change than that indicated by these equations involving loss of weight took place. As a matter of fact, other changes actually do take place, and these involve a slight loss of weight. The latter fact is shown by the following numbers:

Sample.		Non-fatty solids, per cent.	Sample.		Non-fatty solids, per cent.
No. 1.	Fresh milk	8·97	No. 9.	Fresh milk	9·27
	After 4 weeks	8·74		After 11 weeks	8·91
	,, 7 ,,	8·61	No. 10.	Fresh milk	9·11
	,, 12 ,,	8·49		After 13 weeks	8·24
No. 2.	Fresh milk	8·99	No. 11.	Fresh milk	9·34
	After 4 weeks	8·60		After 13 weeks	9·01
No. 3.	Fresh milk	9·12	No. 12.	Fresh milk	8·42
	After $14\frac{1}{2}$ weeks	8·88		After 13 weeks	8·14
No. 4.	Fresh milk	9·02	No. 13.	Fresh milk	8·83
	After 6 weeks	8·56		After 13 weeks	8·56
No. 5.	Fresh milk	9·02	No. 14.	Fresh milk	9·20
	After $7\frac{1}{2}$ weeks	8·76		After 13 weeks	8·80
	,, 11 ,,	8·53	No. 15.	Fresh milk	9·52
	,, 13 ,,	8·35		After 2 weeks	9·33
No. 6.	Fresh milk	9·13		,, 4 ,,	9·29
	After 8 weeks	8·88		,, 6 ,,	9·32
No. 7.	Fresh milk	9·52		,, 8 ,,	9·22
	After $10\frac{1}{2}$ weeks	9·25			

After the addition of 10 per cent. of water:

Sample.		Non-fatty solids, per cent.	Sample.		Non-fatty solids, per cent.
No. 1.	Fresh milk	8·14	No. 2.	Fresh milk	8·24
	After 2 weeks	7·96		After $5\frac{1}{2}$ weeks	7·88
	,, 4 ,,	7·81			

After the addition of 25 per cent. of water:

Sample.		Non-fatty solids, per cent.	Sample.		Non-fatty solids, per cent.
No. 1.	Fresh milk	7·70	No. 2.	Fresh milk	7·63
	After 2 weeks	7·57		After 2 weeks	7·52
	,, 4 ,,	7·52		,, 4 ,,	7·40
	,, 6 ,,	7·41		,, 6 ,,	6·95
	,, 8 ,,	7·47			

Similar observations, made with unwatered separated milks containing about 0·1 per cent. of fat, gave the following results:

		Per cent.			Per cent.
No. 1.	Fresh milk	9·66	No. 3.	Fresh milk	8·61
	After 9 weeks	9·35		After 13 weeks	7·93
No. 2.	Fresh milk	8·91			
	After 5 weeks	8·60			

Separated milks containing 10 per cent. of added water:

		Per cent.
No. 1.	Fresh milk	8·18
	After 3 weeks	7·86
	,, 57 ,,	6·71
No. 2.	Fresh milk	7·67
	After 3 weeks	7·22
	,, 55 ,,	6·24
No. 3.	Fresh milk	7·76
	After 10½ weeks	7·11
No. 4.	Fresh milk	7·80
	After 26½ weeks	6·22
	,, 27 ,,	6·19

These observations serve to show beyond any doubt that, concurrently with the formation of lactic acid, there are produced substances which are either gaseous at ordinary temperatures, or are volatilised during the operation of determining the non-fatty contents of the sour milk. The aggregate weight of these substances, either gaseous or so volatilised, is not very large, but it is sufficient to affect any estimation of the degree of sophistication to which the milk may have been subjected.

It remains now to ascertain what these substances are, what is their amount, and if, when they are accounted for, it may not still be possible to deduce a trustworthy inference of the character of the original milk.

The fact that butyric acid may be formed in the souring of milk has long been known. Pasteur, in 1861, showed that it may be derived from lactic acid by a special organism (" *vibrion butyrique* "), and since that time a number of observers—for example, Prazmowski, Gruber, and Winogradsky—have described various species of *Clostridium* and other organisms which are capable of producing butyric acid under suitable conditions.

It is not improbable, therefore, that a certain, although possibly a relatively small, amount of lactic acid is transformed under certain conditions into butyric acid, even in the comparatively early stages of the souring of milk.

It is, however, certain that milk in which the butyric stage of fermentation has become very pronounced is of relatively infrequent occurrence in the samples received for analysis at the Government Laboratory.

On the other hand, acetic acid is almost invariably present in such examples. The amount is never very large, and seldom exceeds 0·2 per cent., even at the end of a month. In the series of the eight experiments previously mentioned, the percentage amount of the total volatile acids formed during the souring of the several samples, four in the case of each milk, was as follows:

Volatile acids, calculated as acetic acid.

	No. 1.	2.	3.	4.	5.	6.	7.	8.	
At end of 2 weeks......	0·13	0·12	0·11	0·19	0·13	0·10	0·13	0·10	per cent.
,, 4 ,, ...	0·10	0·32	0·16	0·14	0·10	0·35	0·11	0·17	,,
,, 6 ,, ...	0·13	0·46	0·28	0·17	0·12	0·37	0·13	0·18	,,
,, 8 ,, ...	0·09	0·54	0·55	0·36	0·10	0·36	0·26	0·47	,,

In the second month, the presence of butyric acid was more marked in certain of the samples, as in the second and third samples, where the maximum numbers were 0·54 and 0·55 per cent.

The precise mechanism of the production of the volatile acids in the sour milk is not very clear. Butyric acid is generally assumed to be derived from lactic acid in accordance with the equation—

$$2CH_3{\cdot}CH(OH){\cdot}CO_2H = CH_3{\cdot}[CH_2]_2{\cdot}CO_2H + 2CO_2 + 2H_2.$$

The acetic acid may arise either from the oxidation of lactic acid or of ethyl alcohol, which, as we shall see, is an almost invariable constituent of soured milk.

$$CH_3{\cdot}CH(OH){\cdot}CO_2H + O_2 = CH_3{\cdot}CO_2H + CO_2 + H_2O$$
$$CH_3{\cdot}CH_2{\cdot}OH + O_2 = CH_3{\cdot}CO_2H + H_2O.$$

For each molecule of acetic acid produced there is formed in the one case a molecule of carbon dioxide and a molecule of water; and in the other case only a molecule of water. In the latter instance, however, a molecule of carbon dioxide has already been lost in the production of the alcohol, so that the resultant loss is the same in either case.

In the formation of a molecule of butyric acid from lactic acid there are formed two molecules of carbon dioxide and two molecules of hydrogen.

Of course, in the actual conduct of the analysis, any acetic and butyric acids, as well as any small quantity of dissolved carbonic acid, present are neutralised by the strontia used preparatory to evaporation, and are weighed with the non-fatty solids. What is not weighed is the carbon dioxide which has escaped from the soured milk before neutralisation, together with the water and free hydrogen which may be formed indirectly out of the lactose.

As already stated, ethyl alcohol is an almost invariable concomitant of the fermentative changes which occur in milk kept under such conditions as we are here concerned with. In experiments made upon specially procured samples of milk known to contain no alcohol when in the fresh state, alcohol was always formed after a week or two; and out of several hundreds of samples examined under the provisions of the Sale of Food and Drugs Acts the cases have been very few in which alcohol could not be detected. The quantities formed during the eight series of experiments already referred to were as follows:

Alcohol, calculated as ethyl alcohol.

	No. 1.	2.	3.	4.	5.	6.	7.	8.	
At end of 2 weeks	0·060	0·129	0·021	0·042	0·042	0·105	0·012	0·048	per cent.
,, 4 ,,	0·078	0·132	0·054	0·060	0·051	0·108	0·039	0·087	,,
,, 6 ,,	0·060	0·162	0·093	0·087	0·096	0·135	0·342	0·093	,,
,, 8 ,,	0·090	0·156	0·090	0·222	0·071	0·126	0·354	0·204	,,

The production of small quantities of alcohol in cow's milk when kept without the addition of any special ferment has also been remarked by other observers (Vieth, *Analyst*, 1887, **12**, 2; Kingzett, *ibid.*, 234; Kozai, *Zeit. Hyg. Inf.*, 1901, **38**, 386). In some cases, however, the evidence offered has not conclusively proved that the substance in question was alcohol; thus U. and O. Henzold (*Milch Zeit.*, 1901, **30**, 181) object to all proofs that are based on the iodoform reaction alone.

The conversion of lactose into alcohol, although it does not occur with ordinary yeast, has been shown by Lorin (*Zeit. anal. Chem.*, 1879, **18**, 107) to be effected by certain species of *Schizomycetes*. It has been given as occurring in the two stages:—

$$(1)\quad \underset{\alpha\text{-Lactose.}}{C_{12}H_{22}O_{11},H_2O} = \underset{d\text{-Glucose.}}{C_6H_{12}O_6} + \underset{d\text{-Galactose.}}{C_6H_{12}O_6}$$

$$(2)\quad \underset{d\text{-Glucose.}}{C_6H_{12}O_6} = 2C_2H_5{\cdot}OH + 2CO_2.$$

Tollens and Stone, however, have shown (*Ber.*, 1888, **21**, 1572) that galactose is completely fermentable if the necessary food for the micro-organisms is present, so that in the case of lactose in milk the reaction may, perhaps equally well, be expressed as:—

$$C_{12}H_{22}O_{11},H_2O = 4C_2H_5{\cdot}OH + 4CO_2.$$

Moreover, ordinary yeast ferments are known to be occasionally present in samples of market milk, especially as exposed for sale in large towns; it is not improbable, therefore, that these may directly attack the *d*-glucose produced in the course of the change of the lactose to lactic acid.

In any case, the production of one molecule of alcohol corresponds to the elimination of one molecule of carbon dioxide, so that the decrease of weight in the lactose due to the production of these two volatile compounds is $=90/46$ times the weight of the alcohol produced.

In ordinary alcoholic fermentation, it is well known that a small proportion of the fermented sugar, about one-twentieth of the whole, is not converted into ethyl alcohol. The chief by-products are higher alcohols, glycerol, and succinic acid. Assuming that this or something analogous occurs also in the production of alcohol from milk, it is to be remarked that the by-products can have no sensible effect on the conclusions drawn from the quantity of alcohol present. Since the main product is itself but small, the by-products are, for practical purposes, negligible; moreover, they are already partly taken account of in the analysis, since any traces of higher alcohols are weighed with the ethyl alcohol, and succinic acid is neutralised and weighed with the solid matter.

Turning now to the proteids; the ordinary "curdling" of milk in the early stages is a simple precipitation of the casein, due to the interaction of the lactic or acetic acid with the calcium compound of the proteid. But proteolytic changes may also occur, consequent on the development of enzyme-forming bacteria. These changes result in the conversion of a portion of the casein and albumin into proteoses and peptones, giving at a later stage amino-compounds, such as leucine, lysine, and tyrosine. A small quantity of ammonia and amine bases may also be produced.

Profound as these changes are, their net effect on the weight of the proteids, under such conditions as we are here concerned with, is relatively insignificant. It must be borne in mind that the whole of the products mentioned, with the possible exception of traces of ammonia and amines, are weighed with the unchanged casein and other non-fatty solids in the course of the analysis. It is only a question of the change of total weight involved in the conversion of the protein molecule into the simpler compounds indicated above. On the one hand, there may be a gain of weight due to the absorption of the elements of water in the hydrolysis of the casein molecule; on the other hand, there may be a loss, consequent on the ultimate conversion of a portion of the casein into carbon dioxide, ammonia, and water.

However this may be, experimental evidence shows that, as regards its effect upon the weight, the net result of these changes is usually very small. The total loss of solid matter from all causes whatever ranges, as a rule, only from 0·2 to 0·5 per cent., and nearly the whole of this is accounted for by the transformation of lactose into alcohol and volatile acid. A few typical examples will illustrate this; the first series relates to unwatered milk, the second to milk containing approximately 25 per cent. of added water.

Non-fatty solids.				Accounted for by alcohol and volatile acid.	Deficiency, including loss due to change in proteids.
Fresh milk.	Sour milk.		Loss.		
9·52	2 weeks old	9·33	0·19	0·16	0·03
,,	4 ,,	9·29	0·23	0·18	0·05
,,	6 ,,	9·32	0·20	0·17	0·03
7·70	2 ,,	7·57	0·13	0·13	0·00
,,	4 ,,	7·52	0·18	0·14	0·04
,,	6 ,,	7·41	0·29	0·22	0·07

Determinations of the amounts of ammonia produced in the eight series of experiments previously referred to showed that the percentage of ammonia (including amines as estimated by Nesslerising) ranged from 0·001 to 0·012 per cent. during the eight weeks covered by the experiments. These quantities correspond, at most, to a

loss of proteids ranging from 0·006 to 0·075 per cent., and for practical purposes are almost negligible.

In order to obtain further knowledge of the nature and amount of the substances produced in the souring of milk under the conditions in which reference samples are usually kept, the following experiments were made:—

About twenty gallons of milk was mixed with one-fourth of its volume of water, placed in stoppered bottles, and kept at a mean temperature of about 18° during a period of ten to twelve weeks. At the end of that time the acid liquid was distilled, the distillate made alkaline, and re-distilled. The distillation was again repeated, the liquid being rendered alternately acid and alkaline and concentrated by means of a fractionating column. Eventually the alcoholic distillate was rectified successively over potassium carbonate and lime, and finally distilled after long standing over quick-lime.

By this means a total quantity of 76·4 grams of ethyl alcohol was separated from the sour milk. That this was ethyl alcohol was proved by the following facts: It distilled completely between 78·2° and 78·6° (corr.) and chiefly between 78·3° and 78·5° (corr.). Its specific gravity at 15·5°/15·5° was 0·7935. Ten c.c. of the alcohol, treated with 15 grams of iodine and 2 grams of phosphorus, yielded 8 c.c. of alkyl iodide, from which on rectification 7 c.c. were obtained distilling completely between 71·1° and 71·8° (corr.), and which consisted, therefore, of practically pure ethyl iodide. A portion of the alcohol, converted into its *m*-dinitrobenzoic ester, yielded white needles melting at 92·6° (corr.), corresponding to the melting point of ethyl *m*-dinitrobenzoate. There is no question, therefore, that ethyl alcohol is one of the products of the souring of milk when kept under ordinary conditions.

The solution of sodium salts of the volatile acids obtained in the distillation was concentrated, acidified, and extracted with light petroleum. On distilling off the solvent and fractionating the dissolved acids, a large quantity of *n*-butyric acid was obtained. The total amount of this acid, including a small quantity yielded by the subsequent operations, was approximately 390 grams; of this, 300 grams were separated as the nearly pure acid, and the remainder was contained in the intermediate fractions.

The following data characterise this product as *n*-butyric acid: b. p. 162° to 163·5° (corr.); m. p. of the *p*-toluidide, 73·7°. 0·4900 gram of the barium salt gave 0·3674 gram of $BaSO_4$, corresponding to Ba = 44·13 per cent.; barium butyrate requires Ba = 44·11 per cent.

The aqueous-acid liquid from the light petroleum extraction contained a little butyric acid, possibly propionic acid, and the greater portion of the lower homologues. It was neutralised, evaporated to dryness, and a portion of the sodium salts tested qualitatively for formic acid. No evidence of the presence of this acid could be obtained. The sodium salts were, therefore, distilled with slightly diluted sulphuric acid, and the resulting volatile acids fractionated to remove as much of the butyric acid as practicable; the remainder was then treated with lead oxide and examined by Linnemann's method, but no definite evidence could be obtained of the presence of propionic acid. Eventually, by fractional neutralisation and distillation, we obtained an aqueous solution of nearly pure acetic acid, and intermediate fractions, which contained acetic and butyric acids and possibly a little propionic acid. The acetic acid was definitely characterised by its *p*-toluidide, which, after two crystallisations from boiling water and one from benzene, melted at 147·8° (corr.). (The m. p. of pure aceto-*p*-toluidide is variously given as 148·2° and 153°.) 0·2184 gram of the barium salt prepared from the acid gave 0·1976 gram of $BaSO_4$; Ba = 53·2 per cent.; whereas $(C_2H_3O_2)_2Ba$ requires Ba = 53·8 per cent. The total quantity of acetic acid was calculated to be approximately 116 grams, or between one-fourth and one-fifth of the whole amount of volatile acid.

A small quantity, less than 2 grams, of an acid having a higher molecular weight than butyric acid was also obtained. Its barium salt contained 30·5 per cent. of barium, corresponding closely to the salt of a nonoic acid; but since its boiling point was not constant, the fraction was considered to be a mixture of homologues. The quantity, however, is less than 1/200th part of the total acids, and in the present connection is of no practical importance.

The acids of which we have certainly established the existence in the sour milk are acetic and buytric; if any propionic acid is present, it can only be present to the extent of insignificant traces.

A reserved portion of the fermented milk was filtered from fat and coagulated casein, and neutralised with alkali; a precipitate of acid-albumin was given. The proteids in solution (albumoses and peptones) were precipitated with tannic acid and sodium chloride, allowed to deposit, an aliquot part of the supernatant liquid passed through a filter, and distilled with magnesia to separate any volatile bases from the amino-acids which might be present in the solution. The distillate was received in an excess of hydrochloric acid, and evaporated to dryness; from 100 c.c. of the milk-serum 0·136 gram of chlorides was obtained. On treatment of the chlorides with "absolute" alcohol 0·074 gram was dissolved The

dissolved portion was proved by the analysis of its platinichloride to consist largely, and the undissolved residue entirely, of ammonium chloride:

Dissolved portion: 0·0479 platinum salt gave Pt = 0·0208, Pt = 43·4 per cent. Residual portion: 0·0452 platinum salt gave Pt = 0·0198, Pt = 43·8 per cent.; $(NH_4)_2PtCl_6$ requires Pt = 43·9 per cent.

From these numbers it follows that practically the whole of the volatile base consists of ammonia.

A determination of the ammonia by Nessler's method, carried out on the filtered milk without separation of the albumoses or distillation, gave a result corresponding to 0·134 gram of ammonium chloride per 100 c.c., agreeing substantially with the gravimetric determination.

Hence, therefore, it may be considered proven that by far the greatest proportion of the volatile products of the fermentation of milk, other than water and carbon dioxide, are ethyl alcohol, acetic and butyric acids, and a small quantity of ammonia. A small proportion of higher acids, possibly traces of propionic acid, and of volatile organic bases may also be produced. But the amount of these by-products, in comparison with the main quantities, is, in any case, so small that in the present connection they are of no practical significance.

The experimental evidence thus detailed enables us to deal with the practical question involved in this inquiry, which is, whether it is practicable, from a study of the changes which occur in milk during the process of souring, to ascertain, with sufficient accuracy for the purposes of justice, what was the proportion of non-fatty solids in the original milk.

In this connection two remarks may be made. First, the great majority of samples dealt with are only fermented to a relatively small extent; they are between three and six weeks old, have been preserved in sealed bottles containing only a limited quantity of air, and the total diminution in weight of their non-fatty solids, due to the formation of volatile products, is usually only a few tenths of 1 per cent.—from 0·2 to 0·5 in fact. Therefore, the question in its practical aspect does not involve the more considerable changes which, no doubt, may be produced in milk by long-continued fermentation under other conditions. Secondly, in ordinary careful determinations of the non-fatty solids in the same sample of fresh milk by different persons, the results may frequently differ by 0·1 to 0·2 per cent.

For instance, on p. 392 of the "Minutes of Evidence," taken before a Departmental Committee appointed to consider regulations

for milk and cream (Blue Book, 1901, Cd. 484), the results are given of some specially-devised test-experiments, arranged to indicate the effect of "personal equation," and carried out by three well-known operators. The mean values of the average results obtained by each analyst for the non-fatty solids in certain samples of milk are 8·88, 8·79, and 8·90 per cent., showing a maximum difference of 0·11 per cent. The mean values of the separate results show differences exceeding 0·2 per cent. in some cases.

Consequently, in deciding what may be considered as "sufficient accuracy" in the present connection, it may fairly be assumed that an agreement of the calculated non-fatty solids with the original quantity to 0·1—0·2 per cent. is a satisfactory result. An error of 0·1 per cent. corresponds to an error of about 1 per cent. in calculating the amount of added water.

The analysis of milk in the case of samples referred to the Government Laboratory is conducted by what is known as the "maceration" process, and the weight of the non-fatty solids and fat is independently ascertained in duplicate experiments, whilst as a control a direct determination of the total solids is made on a third portion of the milk.

From the judicial standpoint, it is obviously desirable that the quantity of any constituent on which a legal charge may be based should be determined by direct weighing rather than by difference. The "maceration" process is the only method applicable to sour milks which leaves the residual non-fatty solids in a convenient form for accurate weighing. The trustworthiness of the determinations of fat by this method has been completely established in the Government Laboratory. It has been repeatedly proved, by direct and independent experiments, that when the process is conducted in the manner described (p. 220), practically the whole of the fat is extracted and is obtained in a form admitting of accurate determination. Comparison with other methods has also been made; thus the following results were obtained, generally by two analysts working independently, in ascertaining the amount of fat in forty samples of milk, both by the "maceration" process and by the method known as the "Werner-Schmid" process:

	Percentages of fat.								
Maceration	2·59	2·78	1·91	2·15	1·64	2·74	2·53	2·76	2·94
Werner-Schmid	2·59	2·88	1·91	2·33	1·71	2·73	2·52	2·77	2·86
Maceration	2·04	2·48	3·76	2·79	3·18	8·64	2·64	5·18	2·39
Werner-Schmid	2·02	2·48	3·73	2·73	3·14	8 78	2·55	5·22	2·41
Maceration	3·79	3·10	2·94	2·08	2·59	3·49	2·68	2·48	
Werner-Schmid	3·79	3·15	2·86	2·09	2·54	3·51	2·69	2·49	
Maceration	2·73	2·44	3·11	4·05	2·13	3·56	2·39	2·74	
Werner-Schmid	2·73	2·44	3·16	4·04	2·01	3·41	2·36	2·71	
Maceration	2·85	2·65	2·95	0·63	2·54	2·48			
Werner-Schmid	2·78	2·62	2·81	0·55	2·53	2·41			

The Werner-Schmid method of determining the fat is admittedly liable to certain small errors, but as these tend to compensate each other, it is generally accepted by public and other analysts as yielding substantially accurate results (Richmond, *Dairy Chemistry*, p. 99—100; Winter Blyth, *Foods, their Composition and Analysis*, p. 221; Allen, *Commercial Organic Analysis*, Vol. IV., p. 135). Comparison of the "maceration" process with other standard methods has been specially made by independent observers; thus Richmond (*Dairy Chemistry*, pp. 94—96) remarks that "the determination of fat (by the 'maceration' process) [on fresh milk] has proved, in the author's hands, to be accurate, as is shown by the following figures of determinations of fat by the Bell (maceration) and Adams methods respectively:

"Fat, Bell	4·28	4·61	0·19	2·69	3·13	3·45	3·00	8·03	4·16
"Fat, Adams	4·29	4·59	0·30	2·61	3·09	3·42	3·05	8·21	4·21"

The results of another series of test-experiments, carried out by three analysts independently, on nine samples of fresh milk with the view of indicating the variations between the results given by several methods, are given in detail on p. 391 of Blue Book, Cd. 484 (Minutes of Evidence, Departmental Committee on Milk and Cream Regulations). The mean figures for all the fifty-four analyses are as follows:

Method.	Fat, per cent.	Method.	Fat, per cent.
Adams (dry ether)	3·76	Maceration	3·77
,, (commercial ether) ...	3·78	Centrifugal.........................	3·72
Werner-Schmid..................	3·88	Centrifugal (R)	3·72

Here the figure yielded by the maceration method is exactly the average of all the others, and is practically the same as that given by the two "Adams" methods.

Before proceeding with the analysis of a sample of sour milk in the Government Laboratory, the contents of the bottle are transferred to a suitable vessel and thoroughly mixed with a wire whisk.

Portions of the sample, about 10 grams in each case, are weighed out into flat-bottomed platinum capsules, each of which has been tared along with a short glass rod having a flattened end. All the weighings and measurements are independently checked by two analysts. The weighed quantities are next neutralised with $N/10$ solution of strontia, using phenolphthalein as indicator.

The milk is then evaporated over the water-bath until the residue, which towards the end should be dried at a very gentle heat and with constant stirring, attains the consistency of dry cheese. About 20 c.c. of dehydrated ether are poured over the milk solids, which

are then carefully triturated with the glass rod. The ethereal solution of the fat is passed through a filter, which has previously been dried and weighed in a weighing-bottle, and the maceration of the milk is continued with eight successive quantities of ether. At the conclusion of the process, the non-fatty solids should be in a fine state of division resembling the precipitated chalk of pharmacy. Before becoming quite dry, the solids are transferred, as far as practicable, to the weighing bottle, the filter-paper, washed free from fat, is replaced in the bottle, and the whole, with the platinum capsule containing the small adherent quantity of solids, is dried at 100° for three hours, and weighed. The weight is again taken after drying for a further two hours, and a final confirmatory weighing after another hour; the two last weights should not differ by more than a milligram. Deducting 0·00428 gram for each c.c. of $N/10$ strontia used in the neutralising, the result gives the amount of non-fatty solids actually present in the quantity of milk taken for the analysis.

The ethereal solution of the milk-fat is received in small tared flasks; from these the ether is distilled and the weight of the dried fat ascertained.

As regards the alcohol, 50, 75, or 100 grams of the milk are distilled, and the distillate re-distilled after being neutralised with $N/10$ caustic soda solution, litmus paper being used as the indicator. The specific gravity of the distillate, made up to the original or other convenient bulk, is determined in a 50 gram pycnometer, and the quantity of alcohol corresponding to this specific gravity is deduced from a table. The percentage by weight of alcohol, multiplied by 90/46, gives, as already explained (p. 213), the percentage amount of lactose which has disappeared in the production of the alcohol.

As regards the experimental error involved in determining small amounts of alcohol by means of the pycnometer, it may be remarked that many thousands of such determinations are made every year in the Government Laboratory. The experience thus gained shows that in well-conducted experiments the differences obtained in successive tests of the same liquid—this liquid containing alcohol in about the same proportion as is found in sour milk—would rarely or never exceed 0·00002, in terms of specific gravity, and usually would not be more than 0·00001. The higher of these figures would, in the case of milk, correspond to about 0·02 per cent. of non-fatty solids.

The amount of volatile acid is ascertained as follows: 10 grams of the milk, contained in a platinum capsule, are neutralised to the extent of one-half the total acidity (previously determined on

another portion) with $N/10$ caustic soda, and a little phenolphthalein added. The mixture is then evaporated to dryness on a water-bath with frequent stirring, and after treatment with about 20 c.c. of boiling distilled water so as to break up and thoroughly detach the milk solids from the capsule, a further addition of $N/10$ caustic soda is made, until the neutral point is reached. The difference between the original acidity of the milk and that of the evaporated portion is regarded as acetic acid. As previously shown, the production of each molecule (60 parts) of this acid denotes a loss of one molecule of carbon dioxide and one of water, that is, a loss of 62 parts of the original lactose.

When it is desired to take account of any butyric acid that may be present, the volatile acids are separated by distillation from the quantity of milk which has been taken for the determination of the alcohol. A portion of the mixed aqueous acids is neutralised with barium hydroxide, evaporated, and dried until the weight is constant. From the percentage of barium contained in the mixed salts, the proportions of the two acids are calculated. Each molecule of butyric acid (88 parts) denotes a loss of 92 parts of lactose; the loss of lactose due to the formation of acetic acid is calculated as before.

To estimate the small quantity of ammonia formed, 2 grams of the milk are made up to a volume of 100 c.c. with distilled ammonia-free water, and filtered through a carefully-washed filter. In 10 c.c. of the clear filtrate, increased to 50 c.c. by the addition of distilled water, the ammonia is determined by Nessler's method, using a standard solution of ammonium chloride containing 0·01 milligram of ammonia per c.c.

Applying the foregoing principles to the examination of a number of samples of milk kept under observation in the Government Laboratory, we give first the results of experiments, made by several observers, in cases where the milk did not develop the butyric fermentation, or only to an insignificant degree.

TABLE I.—*Unwatered Whole Milks.*

Sample.	Time kept. Weeks.	Loss of non-fatty solids. (1) Actual. Per cent.	(2) Calculated from the experimental determinations of alcohol, acid, and ammonia. Per cent.	Difference between the actual loss and that calculated. Per cent.
No. 1 ...	3	0·26	0·20	−0·06
,, ...	4	0·23	0·21	−0·02
,, ...	7	0·36	0·34	−0·02
,, ...	12	0·48	0·49	+0·01
No. 2 ...	4	0·39	0·35	−0·04
No. 3 ...	6	0·30	0·33	+0·03
,, ...	14½	0·24	0·25	+0·01
No. 4 ...	6	0·46	0·58	+0·12
No. 5 ...	7½	0·26	0·20	−0·06
,, ...	11	0·49	0·49	0·00
,, ...	13	0·67	0·61	−0·06
No. 6 ...	8	0·25	0·23	−0·02
No. 7 ...	10½	0·27	0·35	+0·08
No. 8 ...	11	0·36	0·32	−0·04
No. 9 ...	13	0·87	0·76	−0·11
No. 10 ...	13	0·33	0·41	+0·08
No. 11 ...	13	0·28	0·26	−0·02
No. 12 ...	13	0·27	0·31	+0·04
No. 13 ...	13	0·40	0·39	−0·01
No. 14 ...	2	0·19	0·16	−0·03
,, ...	4	0·23	0·18	−0·05
,, ...	6	0·20	0·17	−0·03
,, ...	8	0·30	0·20	−0·10

TABLE II.—*Watered Whole Milks.*

(1) Approximately 10 per cent. of water added:

Sample.	Time kept. Weeks.	Loss of non-fatty solids. (1) Actual. Per cent.	(2) Calculated from the experimental determinations of alcohol, acid, and ammonia. Per cent.	Difference between the actual loss and that calculated. Per cent.
No. 1 ...	2	0·18	0·27	+0·09
,, ...	4	0·33	0·42	+0·09
No. 2 ...	5½	0·36	0·43	−0·03
,, ...	5½	0·51	0·50	−0·01

(2) Approximately 25 per cent. of water added :

No. 1 ...	2	0·13	0·13	0·00
,, ...	4	0·18	0·14	−0·04
,, ...	6	0·29	0·22	−0·07
,, ...	8	0·23	0·19	−0·04
No. 2 ...	2	0·11	0·08	−0·03
,, ...	4	0·23	0·12	−0·11
,, ...	6	0·68	0·63	−0·05

TABLE III.—*Unwatered Separated Milks.*

Sample.	Time. kept. Weeks.	Loss of non-fatty solids. (1) Actual. Per cent.	(2) Calculated from the experimental determinations of alcohol, acid, and ammonia. Per cent.	Difference between the actual loss and that calculated. Per cent.
No. 1 ...	4	0·41	0·22	−0·19
,, ...	5	0·32	0·13	−0·19
,, ...	9	0·31	0·26	−0·05
No. 2 ...	4	0·29	0 28	−0·01
,, ...	5	0·31	0·20	−0·11
No. 3 ...	4	0 28	0·24	−0·04
,, ...	5	0·32	0·28	−0·04
,, ...	13	0·68	0·58	−0·10

TABLE IV.—*Watered Separated Milks.*

Approximately 10 per cent. of water added:

Sample.	Time kept. Weeks.	Loss of non-fatty solids. (1) Actual. Per cent.	(2) Calculated from the experimental determinations of alcohol, acid, and ammonia. Per cent.	Difference between the actual loss and that calculated. Per cent.
No. 1 ...	3	0·32	0 24	−0·08
,, ...	55	1·47	1·50	+0·03
,, ...	55	1·54	1·56	+0·02
,, ...	57	1·47	1·50	+0·03
No. 2 ...	3	0·45	0·33	−0·12
,, ...	55	1·43	1·49	+0·06
No. 3 ...	10½	0·65	0·55	−0·10
No. 4 ...	26½	1·58	1·59	+0·01
,, ...	27	1·61	1·69	+0·08

In nearly all the foregoing cases, it will be seen that the actual amount of original non-fatty solids has been very closely ascertained from the experiments on the milks, although the period of keeping was sometimes very prolonged, and in four instances extended to more than a year. The difference between the calculated and the actual amount is usually not greater than might be obtained in duplicate determinations made by the same operator on the fresh sample, and in only two cases does it appreciably exceed the difference which, as has been pointed out, two careful analysts might obtain with the same sample. The amount of added water, whether 10 per cent. or 25, has in all cases been correctly indicated to within about 1 per cent. by the analysis of the fermented milk. It should be added that, in order to assimilate the conditions to something like the worst which would be found in practice, the larger quantity (25

per cent.) of water was in one series of experiments a much-polluted water obtained from the Old Fleet River.

Milk in which the butyric stage of fermentation has become very pronounced is of relatively infrequent occurrence amongst the samples received. Where the decomposition is considerable and much acid has been formed, it is sometimes difficult, on account of the separated casein, to get the sample into a uniform condition for analysis. Where this is so, the analysis is not proceeded with. But as far as the butyric acid itself is concerned, the analysis can be carried out on the principles already explained, if the relative proportions of butyric and acetic acids are determined by some convenient method, such as the analysis of the barium salts given by the mixed acids. That this can be done with a good approach to accuracy is shown by the following experiments carried out on milk in which a large proportion of butyric acid was eventually formed.

TABLE V.

			Loss of non-fatty solids.		
Sample.	Time kept. Weeks.	Butyric acid. Per cent.	Actual. Per cent.	Calculated from the experimental determinations of alcohol, acid, and ammonia. Per cent.	Difference between the actual loss and that calculated. Per cent.
No. 1 ...	4	0·33	0·66	0·67	+0·01
,, ...	6	0·59	1·03	0·95	−0·08
,, ...	8	0·55	0·86	0·90	+0·04
No. 2 ...	6	0·23	0·65	0·41	−0·24
Watered Milk.	Approximately 25 per cent. of water added:				
No. 3 ...	4	0·17	0·34	0·22	−0·12
,, ...	6	0·28	0·69	0·53	−0·16
,, ...	8	0·66	1·39	1·10	−0·29
No. 4 ...	4	0·40	0·71	0·67	−0·04
,, ...	6	0·56	1·00	0·89	−0·11
,, ...	8	0·30	0·60	0·58	−0·02

In most of these cases, the amount of added water is indicated correctly to within about 1 per cent., although in one instance 3 per cent. more water than was added would be indicated. For practical purposes, however, such an exceptional case is of little consequence; the offence is substantially the same whether the quantity of water added to the milk be 25 per cent. instead of 28; or whether it be 15 instead of 18 per cent.

This communication is based on experimental work accumulated by a number of analysts in the Government Laboratory, mainly during the past ten years, and notably by Mr. George Lewin, Mr.

John Holmes, sen., Mr. Cameron, Mr. Chas. Proctor, Mr. Wilson Davis, and Mr. Chas. Simmonds. I desire to express my indebtedness to these gentlemen for the skill and patience with which they have assisted me in the course of what has necessarily proved to be a somewhat protracted inquiry.

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XXVII.—*The Nitration of Substituted Azophenols.*

By JOHN THEODORE HEWITT and HERBERT VICTOR MITCHELL.

THE action of substituting agents on azophenols has engaged the attention of several chemists within the last few years (Noelting, *Ber.*, 1887, **20**, 2997; Täuber, *ibid*, 1893, **26**, 1872; Auwers, *ibid.*, 1900, **33**, 1302; Amstrong, Proc., 1899, **15**, 243; Hewitt and Aston, Auld, Fox, Lindfield, Phillips and Tervet, Trans., 1900, **77**, 99, 712, 810; 1901, **79**, 49, 155, 160, 1090; 1902, **81**, 171, 1202). The general result has been to show that *p*-hydroxyazo-compounds nitrate with dilute nitric acid and brominate in presence of sodium acetate and acetic acid in the ortho-position to the hydroxyl group, that is, they behave as might be expected of true azophenols.

On the other hand, Noelting obtained *p*-nitrobenzeneazophenol by acting on benzeneazophenol with one molecular proportion of nitric acid in presence of an excess of concentrated sulphuric acid (*loc. cit.*), whilst with two molecular proportions of nitric acid he states that a product is obtained identical with that produced by the diazotisation of 2 : 4-dinitroaniline and subsequent coupling with phenol. Noelting's statement with respect to the formation of *p*-nitrobenzeneazophenol when one molecule of nitric acid is employed needs no qualification; but with two molecules of nitric acid, if the dinitrobenzeneazophenol is formed at all, it must be in subordinate amount, since when any one of the three nitrobenzeneazophenols is further nitrated, not merely with warm dilute nitric acid, but even in presence of strong sulphuric acid, the second nitro-group enters in the ortho-position to the phenolic hydroxyl.

This corresponds closely to the result obtained by Täuber, who found that both *p*- and *m*-sulphobenzeneazophenols nitrated in the ortho-position to the hydroxyl group in presence of strong sulphuric acid.

The obvious explanation in the case of benzeneazophenol (compare

Auwers, *loc. cit.*) is to regard the free substance as having a constitution corresponding to its name, whilst in strong sulphuric acid solution it exists as a salt of the tautomeric quinonephenylhydrazone. This explanation can be extended to include the observations made by Täuber; a substance having the constitution

$$HSO_3{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH$$

would hardly be basic enough to form a salt of the type

$$HSO_3{\cdot}C_6H_4{\cdot}\underset{H\ \ SO_4H}{NH}{\cdot}N{:}C_6H{:}O ,$$

and thus still preserve its phenolic character and nitrate as a phenol.

Whilst salts with mineral acids have not been obtained in the case where the substituent group is SO_3H, the argument that the nitro-group also hinders salt formation requires some qualification. Hewitt, Moore, and Pitt (*Ber.*, 1898, **31**, 2114) have described hydrochlorides of *m*- and *p*-nitrobenzeneazophenols, so undoubtedly salt formation can take place. The explanation may lie in the diminution of the basicity by the introduction of the nitro-group, so that the solution of the nitrobenzeneazophenol in the strong sulphuric acid is to be looked on as an equilibrium mixture.

$$NO_2{\cdot}C_6H_4{\cdot}N{:}N{\cdot}C_6H_4{\cdot}OH + H_2SO_4 \rightleftharpoons NO_2{\cdot}C_6H_4{\cdot}\underset{H\ \ SO_4H}{NH}{\cdot}N{:}C_6H_4{:}O .$$

Whilst the free azophenol would nitrate instantly, the quinonehydrazone salt on the right-hand side obviously would not nitrate in the quinonoid portion of the molecule, whilst so far as the other nucleus is concerned it would nitrate readily enough, were it not that one negative nitro-group has already entered it.

We advance this view with a certain amount of reserve, seeing that the *o*-azophenols brominate in the phenolic nucleus, although Auwers has considered them to be quinonehydrazones. On the other hand, Jacobson considers the hydrazone formula doubtful, even in the case of the salts which *p*-hydroxyazo-compounds furnish with mineral acids, seeing that he has been able to obtain a stable hydrochloride of *m*-hydroxyazobenzene (*Ber.*, 1903, **36**, 4107).

Experimental.

Preparation of o-*Nitrobenzeneazo*-o-*nitrophenol.*

(*a*) By dilute nitric acid:

Ten grams of *o*-nitrobenzeneazophenol were very finely powdered and introduced into a mixture of 20 c.c. of nitric acid of specific

gravity 1·36, with 60 c.c. of distilled water. The whole was stirred, and gradually warmed up to 50° on the water-bath, when the odour of nitrous fumes became marked and the vermilion shade of the mononitroazophenol gradually gave place to the yellow-brown tint of the dinitro-compound. After half an hour at 50°, the temperature was raised to 60°, and maintained at that point, with stirring, for a further 15 minutes. The resulting paste was next diluted with distilled water, filtered off at the pump, washed free from acid, and dried at 100° and recrystallised from boiling glacial acetic acid, when it melted at 187°.

(*b*) By nitration in strong sulphuric acid solution:

o-Nitrobenzeneazophenol was dissolved in ten times its weight of strong sulphuric acid, and the mixture surrounded by cold water. A very slight excess of the calculated amount (1 mol.) of nitric acid (sp. gr. 1·42), itself diluted with strong sulphuric acid, was gradually added, with stirring. After leaving the mixture overnight, it was gradually poured into a large excess of cold water and stirred vigorously.

The compound which separated was washed at the pump, dried and recrystallised from glacial acetic acid; it melted at 186—187°, and on being mixed with the foregoing specimen, no lowering of the melting point could be detected.

(*c*) In order to prove definitely the constitution of this compound, it was synthesised by coupling an *o*-nitrophenyldiazonium salt with *o*-nitrophenol as follows:

A mixture of 5 grams of *o*-nitroaniline, 10 grams of concentrated sulphuric acid, and a small quantity of water, insufficient to remove the amine from solution, was diazotised by 2·6 grams of sodium nitrite dissolved in 5 c.c. of water. The diazo-solution was poured into an excess of water, and added to an aqueous solution of 5 grams of *o*-nitrophenol and 15 grams of sodium carbonate. Coupling took place fairly easily, the azophenol was precipitated by acid, redissolved in hot caustic soda solution, again precipitated, extracted with cold spirit, and finally recrystallised from glacial acetic acid. This preparation, although of a slightly lighter shade than the specimens prepared by nitration, was obviously identical with them, as it melted at 186° and had no effect on their melting point.

o-Nitrobenzeneazo-*o*-nitrophenol crystallises from pure acetic acid in well-defined, long, deep brown needles; it dissolves easily in acetic acid and pyridine and fairly readily in alcohol; it is slightly soluble in benzene or ethyl acetate, and but sparingly so in ether.

0·1118 gave 19·0 c.c. moist nitrogen at 15° and 748 mm. N = 19·7.

$C_{12}H_8O_5N_4$ requires N = 19·4 per cent.

The *acetyl* derivative, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(NO_2) \cdot O \cdot CO \cdot CH_3$, was prepared by boiling together for one hour in a reflux apparatus 1 gram of the azophenol, 1 gram of fused sodium acetate, and 4 grams of acetic anhydride.

The fused product was thrown into water, collected, and recrystallised from glacial acetic acid, when the substance formed thick, scarlet needles, melting at 119°, easily soluble in ether, ethyl acetate, benzene, pyridine, or acetic acid, and moderately so in alcohol.

0·1677 gave 0·3137 CO_2 and 0·0453 H_2O. C = 51·0 ; H = 3·0.
$C_{14}H_{10}O_6N_4$ requires C = 50·9 ; H = 3·0 per cent.

The *benzoyl* derivative, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(NO_2) \cdot O \cdot CO \cdot C_6H_5$, was prepared by boiling the azophenol with enough benzoyl chloride to dissolve it completely, until evolution of hydrochloric acid ceased; the solution was stirred into dilute alcohol, the crude benzoyl derivative was filtered off at the pump and recrystallised from ethyl benzoate. It formed a mass of small, yellow crystals, melting at 174°.

This substance is very soluble in pyridine, moderately so in ethyl acetate, benzene, and acetic acid, very sparingly so in alcohol and ether.

0·1186 gave 0·2548 CO_2 and 0·0346 H_2O. C = 58·6 ; H = 3·2.
$C_{19}H_{12}O_6N_4$ requires C = 58·2 ; H = 3·1 per cent.

Preparation of m-*Nitrobenzeneazo*-o-*nitrophenol.*

(*a*) By means of dilute nitric acid:

The method employed was the same as that indicated in the case of the foregoing isomeride. Ten grams of powdered *m*-nitrobenzeneazophenol and a mixture consisting of 20 c.c. of nitric acid (sp. gr. 1·36) with 60 c.c. of water were warmed on the water-bath, and stirred continuously. In this case, the nitration appeared to take place with somewhat more difficulty; it was found possible to work at about 100°, and even then the reaction was quite moderate.

After 10 minutes at this temperature, the product was collected in the usual way and recrystallised from boiling glacial acetic acid. This specimen melted at 177°.

(*b*) Preparation of the foregoing compound by nitration in strong sulphuric acid solution:

Six grams of *m*-nitrobenzeneazophenol, after being dissolved in 60 grams of strong sulphuric acid, were treated with a cold mixture of 2 c.c. of nitric acid (sp. gr. 1·42) and 10 c.c. of strong sulphuric acid. The addition of the nitric acid was effected gradually, and the temperature of the mixture was not allowed to rise to any appreciable extent. After half an hour, the mixture was poured into a large excess of cold water, the dinitro-compound collected and recrystallised from glacial acetic acid. This specimen also melted

at 177°, and a mixture of it with the preceding preparation had exactly the same melting point. Subsequent crystallisations from chloroform raised the melting point to 179°.

In this particular case, it was considered unnecessary to prove the constitution of the compound by synthesising it from *o*-nitrophenol, as a substance agreeing with it in melting point has been obtained by the rearrangement of di-*m*-dinitroazoxybenzene under the influence of concentrated sulphuric acid (Klinger and Pitschke, *Ber.*, 1885, 18, 2552, and Knipscheer, *Rec. Trav. Chim.*, 1903, 22, 1).

This substance crystallised from chloroform in small, somewhat hard crystals, and readily dissolved in alcohol, benzene, pyridine, and acetic acid; it was less soluble in ethyl acetate, and only slightly so in ether.

0·0951 gave 16 0 c.c. nitrogen at 19° and 774 mm. N = 19·6.
$C_{12}H_8O_5N_4$ requires N = 19·4 per cent.

The *acetyl* derivative, $\langle\ \rangle N{:}N\langle\ \rangle O\cdot CO\cdot CH_3$ (with NO_2 on each ring, as drawn), was obtained

by boiling the azophenol with acetic anhydride and fused sodium acetate in the usual manner; it crystallised from acetic acid in tufts of small, brown crystals which melted at 138°, and were readily soluble in acetic acid or pyridine, moderately so in ether and in ethyl acetate, but only sparingly so in alcohol.

0·1632 gave 24·4 c.c. nitrogen at 15° and 770 mm. N = 17·6.
$C_{14}H_{10}O_6N_4$ requires 17·0 per cent.

The *benzoyl* derivative, $\langle\ \rangle N{:}N\langle\ \rangle O\cdot CO\cdot C_6H_5$ (with NO_2 on each ring, as drawn), was

easily prepared by boiling with benzoyl chloride for one hour; the product was thrown into dilute spirit, and recrystallised from ethyl acetate, when it formed a nearly colourless, crystalline powder melting at 169°. It readily dissolves in pyridine or amyl alcohol, and is moderately soluble in benzene, ether, and ethyl acetate; it is almost insoluble in alcohol.

0·0850 gave 0·1825 CO_2 and 0·0247 H_2O. C = 58·5; H = 3·2.
$C_{19}H_{12}O_6N_4$ requires C = 58·2; H = 3·1 per cent.

Preparation of p-*Nitrobenzeneazo*-o-*nitrophenol*.

(*a*) By the action of dilute nitric acid:

The method previously indicated in the other two cases was employed as regards quantities and dilution of the nitric acid. The

temperature was raised to and maintained at 60° for $1\frac{1}{2}$ hours, when the mass, which had assumed a thick, pasty consistency, was diluted, filtered, and dried, and recrystallised from a considerable quantity of glacial acetic acid. The product separated abundantly on cooling in beautiful, large, red needles and melted at 212°.

(*b*) Preparation from *p*-nitrobenzeneazophenol by nitration in strong sulphuric acid solution:

Finely powdered *p*-nitrobenzeneazophenol was dissolved in a sufficiency of concentrated sulphuric acid, and the calculated quantity (1 mol.) of nitric acid (sp. gr. 1·42) itself, diluted with sulphuric acid, added. The mixture was set aside for a week, then diluted largely, and filtered. The resulting compound, after washing and drying, was recrystallised from hot glacial acetic acid. This specimen melted at 212° and did not depress the melting point of the foregoing specimen.

(*c*) Preparation by coupling *p*-nitrobenzenediazonium salt with *o*-nitrophenol:

Six grams of finely powdered *p*-nitroaniline were mixed with about 50 c.c. of water containing 13 c.c. of fuming hydrochloric acid; the mixture was cooled to 0° by the addition of small pieces of ice, and diazotised by the very gradual addition of a saturated aqueous solution of 3·1 grams of sodium nitrite. The resulting solution was rapidly filtered into one containing 6 grams of *o*-nitrophenol (in the form of its sodium salt) and 20 grams of crystallised sodium acetate with a little sodium carbonate. Coupling took place without delay, and apparently with ease.

The mixture was acidified with hydrochloric acid and the product collected at the pump. As the crude substance thus obtained contained some unaltered *o*-nitrophenol it was mixed with water and distilled in steam in order to remove this substance, and then crystallised thrice from glacial acetic acid. This preparation also melted at 212°, and did not depress the melting point of the specimen prepared by nitration.

p-Nitrobenzeneazo-*o*-nitrophenol crystallises from glacial acetic acid in large, shining, red needles which are only very sparingly soluble in cold acetic acid, and are practically insoluble in alcohol. This substance also dissolves fairly readily in toluene; it is easily soluble in pyridine, and sparingly so in benzene, ethyl acetate, or ether.

0·1399 gave 23·1 c.c. of nitrogen at 19° and 764 mm. N = 19·2.

$C_{12}H_8O_5N_4$ requires N = 19·4 per cent.

The *acetyl* derivative, $NO_2\langle\quad\rangle N_2\langle\quad\rangle O\cdot CO\cdot CH_3$ (with NO_2 on the second ring), was prepared in the usual manner; it crystallised from glacial acetic acid in fine, brown, silky needles, and melted at 138°. This substance is moderately

soluble in ethyl acetate, easily so in benzene, pyridine, and acetic acid, and dissolves less readily in alcohol.

0·1086 gave 0·2028 CO_2 and 0·0286 H_2O. C = 50·9; H = 2·9.
$C_{14}H_{10}O_6N_4$ requires C = 50·9; H = 3·0 per cent.

The *benzoyl* derivative, $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3(NO_2) \cdot O \cdot CO \cdot C_6H_5$, was prepared by boiling the azophenol with benzoyl chloride; it crystallised from ethyl acetate in dark red, small, glistening crystals (m. p. 179°).

This substance is practically insoluble in alcohol, but is soluble in ethyl acetate, and dissolves somewhat sparingly in benzene, pyridine, or acetone.

0·1164 gave 0·2505 CO_2 and 0·0349 H_2O. C = 58·7; H = 3·3.
$C_{19}H_{12}O_6N_4$ requires C = 58·2; H = 3·1 per cent.

Preparation of m-*Nitro*-p-*tolueneazophenol*.

$$CH_3 \cdot C_6H_3(NO_2) \cdot N_2 \cdot C_6H_4 \cdot OH.$$

Three grams of 2-nitro-*p*-toluidine were stirred with the requisite quantity of dilute hydrochloric acid, and the calculated quantity of sodium nitrite, dissolved in water, added, the temperature not being allowed to exceed 0°.

The diazo-solution thus obtained was filtered into a solution of the calculated quantity of phenol with excess of sodium acetate. Coupling proceeded immediately, and the liquid was acidified and filtered. After recrystallisation from glacial acetic acid, the yield was over 4 grams; the product separated from glacial acetic acid in glistening, orange crystals melting at 186°; this substance is readily soluble in acetic acid, ethyl acetate, and pyridine, moderately so in benzene or ether, but scarcely dissolves in alcohol.

0·1593 gave 0·3524 CO_2 and 0·0564 H_2O. C = 60·3; H = 3·97.
$C_{13}H_{11}O_3N_3$ requires C = 60·7; H = 4·3 per cent.

The *acetyl* derivative, $CH_3 \cdot C_6H_3(NO_2) \cdot N_2 \cdot C_6H_4 \cdot O \cdot CO \cdot CH_3$, prepared as in the previous cases, crystallised from dilute acetic acid in fine, golden-yellow needles melting at 113°; it is very soluble in benzene, pyridine, acetic acid, or alcohol, and moderately so in ethyl acetate.

0·1895 gave 0·4200 CO_2 and 0·0720 H_2O. C = 60·4; H = 4·2.
$C_{15}H_{13}O_4N_3$ requires C = 60·2; H = 4·3 per cent.

Preparation of o-*Nitro-p-tolueneazophenol.*

3-Nitro-*p*-toluidine was diazotised and treated with phenol exactly as in the case of its isomeride.

The crude product, after crystallisation from alcohol and two re-crystallisations from benzene, formed small, brown crystals melting at 158°.

0·1179 gave 16·9 c.c. nitrogen at 16° and 764 mm. N = 16·9.
$C_{13}H_{11}O_3N_3$ requires N = 16·4 per cent.

The authors originally intended to prepare, if possible, one of these two tolueneazophenols by the direct nitration in strong sulphuric acid solution of *p*-tolueneazophenol. Experiments in this connection have, so far, led to no very definite conclusion, but this negative result is perhaps not devoid of interest, as it indicates that, in strong acid solution, *p*-tolueneazophenol is not exclusively attacked by nitric acid in any special direction, the para-position in the toluene residue being already occupied by a methyl group.

With dilute nitric acid, this azophenol is obviously most readily substituted in the phenolic nucleus (Hewitt, Lindfield, *loc. cit.*).

All the melting points given in this paper are corrected.

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XXVIII.—*Studies in the Camphane Series. Part XVII. Configuration of* iso*Nitrosocamphor and its Unstable Modification.*

By Martin Onslow Forster.

At the time of describing an unstable modification of *iso*nitroso-camphor (Trans., 1903, **83**, 534, and 1904, **85**, 904), the facts did not justify any decision regarding the configuration of the isomerides; further information has been gained, however, which, taken in conjunction with previous observations, does appear to admit of a definite conclusion being drawn.

Owing to the participation of the group ·CO·C(:NOH)· in the camphane cycloid, the process adopted by Beckmann and Köster (*Annalen*, 1893, **274**, 1) in elucidating the configuration of the benzilmonoximes is not applicable to the *iso*nitrosocamphors; it was necessary, therefore, to seek some other mode of attack, and this has been found in studying the behaviour of these compounds towards magnesium methyl iodide.

In correspondence with the four dioximes of camphorquinone, the existence of which has now been established, it was to be expected that four modifications of the oxime,

$$C_8H_{14}<\begin{matrix}C:NOH \\ | \\ C(OH)\cdot CH_3\end{matrix},$$

would be obtainable on applying the Grignard reaction to the *iso*nitrosocamphors; three of these are described in the present paper, and it is the behaviour of one of them which appears to determine the point in question.

On the basis of the Hantzsch-Werner hypothesis, in association with the requirements of *cis-trans*-isomerism, two modifications of the abovementioned oxime should contain the hydroxyl group of the oximino-substituent in the immediate neighbourhood of the second hydroxyl group, whilst the two remaining forms would have their hydroxyl groups withdrawn from proximity:

I. C_8H_{14} — C(=N·OH)—C(HO)(CH₃)   II. C_8H_{14} — C(=N·OH)—C(HO)(CH₃)

III. C_8H_{14} — C(=N·HO reversed: HO·N)—C(HO)(CH₃)   IV. C_8H_{14} — C(HO·N)—C(HO)(CH₃).

Thus, the oximes having configurations I and II would lend themselves to anhydride formation, whilst modifications III and IV might resist. Now among the three new oximes, all of which are amphoteric, two are converted rapidly into a liquid anhydride when their solutions in dilute acids or alkalis are warmed, whilst the third undergoes the same change in acid, but escapes attack in alkali; as this comparatively indifferent oxime is derived from the unstable *iso*nitrosocamphor, it is reasonable to conclude that the last-named compound has the second of the configurations:

C_8H_{14} — C(=N·OH)—C(=O) C_8H_{14} — C(=N·HO: HO·N)—C(=O),

syn-Modification (m. p. 152°).   *anti*-Modification (m. p. 114°).

the first of which thus represents the stable isomeride.

This aspect of the relationship between the *iso*nitrosocamphors agrees with their behaviour towards benzoyl chloride. It has been shown (Trans., 1904, **85**, 905) that this agent in pyridine converts the unstable *iso*nitrosocamphor into a yellow derivative (m. p. 105°) from which the oximinoketone is regenerated on hydrolysis, whilst the stable modification yields a colourless isomeride (m. p. 136°) hydrolysable to α-camphornitrilic acid. If the stable *iso*nitrosocamphor has the configuration indicated above, in which the hydroxyl group occupies the *syn*-position with respect to carbonyl, circumstances are favourable to the production of *pseudo*-derivatives which would readily yield α-camphornitrilic acid on hydrolysis :

```
  C8H14                    C8H14                  C8H14
   /\                       /\                     /\
 C——C·OBz                 C   C·OH              C——C·OMe
 ||  |         —>        |||  ||       <—      ||  |
 N——O                     N   O                 N——O
```

Colourless benzoyl derivative. α-Camphornitrilic acid. *O*-Methyl ether.

This view of the colourless *pseudo*-derivatives regards them as having the structure which Hantzsch ascribed to the coloured alkali derivatives of α-oximinoketones; without discussing the general question raised by this assumption, it may be pointed out that with respect to *iso*nitrosocamphor, it seems more probable that the coloured alkali derivatives have the normal structure of oximinoketones, whilst the colourless derivatives are of the *pseudo*-type.

Such *pseudo*-compounds might be expected to furnish α-aminocamphor on reduction, since they still contain the camphane ring, and this behaviour has been already noted in connection with the colourless benzoyl derivative and the *O*-methyl ether (*loc. cit.*). The fact that the *pseudo*-derivatives contain the camphor nucleus unimpaired is further demonstrated by their behaviour towards magnesium methyl iodide, which transforms the colourless benzoyl derivative quantitatively into dimethylaminocamphor; this base arises also from the *O*-methyl ether, but the yield is not so good. It is not easy to explain this curious change, which incidentally affords a most convenient process for obtaining dimethylaminocamphor, first prepared by methylating the primary base (Duden and Pritzkow, *Ber.*, 1899, **32**, 1542). In so far as it relates to the behaviour of doubly linked carbon and nitrogen, the reaction is comparable with the observation of Busch (*Ber.*, 1904, **37**, 2691), who converted benzylideneaniline into α-anilinoethylbenzene by means of the Grignard reaction; in this case, however, the added methyl complex becomes attached to carbon, whereas in ψ-benzoyl*iso*nitrosocamphor it is the nitrogen which takes up two of these groups. But the change involves also the removal of oxygen,

and in this respect recalls the replacement of aldehydic oxygen by methyl groups lately noticed by F. Sachs and L. Sachs (*Ber.*, 1905, **38**, 518).

In a recent paper by Werner and Piguet (*Ber.*, 1904, **37**, 4295), prominence has been given to the fact that, in addition to the Beckmann rearrangement of diketone monoximes typified by the change

$$C_6H_5\cdot\underset{N\cdot OH}{\underset{\|}{C}}\cdot CO\cdot C_6H_5 \longrightarrow C_6H_5\cdot\underset{N\cdot CO\cdot C_6H_5}{\underset{\|}{C}}\cdot OH \longrightarrow C_6H_5\cdot\underset{NH\cdot CO\cdot C_6H_5}{\underset{|}{C}}O,$$

there must be recognised a second order of transformation, recalling the behaviour of *syn*-aldoximes,

$$C_6H_5\cdot\underset{N\cdot OH}{\underset{\|}{C}}\cdot CO\cdot C_6H_5 \longrightarrow C_6H_5\cdot\underset{N}{\underset{|||}{C}} + \underset{OH}{\underset{|}{CO}}\cdot C_6H_5.$$

In the case of the *syn*-modification of *iso*nitrosocamphor, the action of benzoyl chloride may be described as an attempt to effect the latter change, which falls short of completion owing to the stability conferred by the camphane nucleus, and is thus arrested at the intermediate stage represented by the *pseudo*-derivative,

```
      C8H14                C8H14               C8H14
     /     \               /   \               /   \
   C ——————— C           C ——— C·OH           C     C·OH
   ‖         ‖    →      ‖     |       →     |||    ‖
 N·OH        O           N ——— O              N     O
 syn-Modification.     pseudo-Derivative.   α-Camphornitrilic acid.
```

As yet the *pseudo*-modification of *iso*nitrosocamphor has been obtained only in the form of its alkyl and acyl derivatives, attempts to isolate the substance itself having always failed owing to the readiness with which alkalis bring about the complete transformation to α-camphornitrilic acid; but it seems highly probable that the colourless compound $C_{20}H_{28}O_3N_2$, obtained by the action of alcoholic ammonia on the colourless (*pseudo*) benzoyl derivative (Trans., 1904, **85**, 907), is the *pseudo*-anhydride,

```
   C8H14       C8H14
   /   \       /   \
  C ——— C·O·C ——— C ,
  ‖     |     |     ‖
  N ——— O     O ——— N
```

isomeric with α-camphornitrilic anhydride and with the yellow anhydride of *iso*nitrosocamphor.

I have lately prepared this compound directly from the *syn*-modification without converting it first into the benzoyl derivative. The transformations described by Werner and Piguet depend on the action

of benzenesulphonic chloride, and Professor Werner having kindly informed me that he did not propose to include *iso*nitrosocamphor in his experiments, I have examined the behaviour of both modifications towards the agent in question. Using pyridine as a medium, it appears that the *syn*-modification yields the colourless anhydride, $C_{20}H_{28}O_3N_2$, referred to above, whilst the *anti*-derivative is transformed into the yellow anhydride (m. p. 194°).

No attempt is made in this communication to determine the configuration of the three isomeric oximes beyond indicating that the α-oxime must be represented by one of the expressions III and IV, whilst the γ-oxime has the configuration I or II. It is noteworthy that although the α- and β-modifications are both derived from the unstable *iso*nitrosocamphor, and both change into the γ-oxime on the water-bath, they should yet be distinguished from one another in their behaviour towards hot alkali; this peculiarity is perhaps explained by the fact that when the α-oxime changes into the γ-isomeride, the β-modification is not produced as an intermediate compound.

Experimental.

The Isomeric Oximes, $C_8H_{14}<\begin{matrix}C:NOH \\ | \\ C(OH)\cdot CH_3\end{matrix}$.

In order to prepare the three oximes by one operation, it is necessary to employ the mixture of *iso*nitrosocamphors produced by the action of amyl nitrite on an ethereal solution of camphor in which sodium has been dissolved, the material thus obtained being recrystallised from boiling water. Twenty grams were added slowly to an ice-cold ethereal solution of magnesium methyl iodide prepared from 50 grams of methyl iodide and 7·2 grams of magnesium; a very vigorous action took place, and the pale yellow powder changed immediately to dark brown lumps, which quickly dissolved. When 15 grams had been added, this product dissolved more slowly, the liquid separating into two layers, of which the lower was dark grey and viscous, the upper being colourless and limpid. After twelve hours, the *iso*nitrosocamphor having disappeared completely, the magnesium compound was decomposed by fragments of ice, and acetic acid in sufficient amount to form a clear solution, which was removed in a separating funnel. The ethereal solution was shaken first with aqueous sodium carbonate, and then with a 5 per cent. solution of potassium hydroxide in quantities of 10 c.c. until the unchanged *iso*nitrosocamphor was removed, about 50 c.c. being required; it was further extracted with 25 per cent. potassium hydroxide, 100 c.c. at a time, until the extract gave no precipitate with acetic acid, 400 c.c. being necessary. The ether was then dried with calcium chloride and evaporated, leaving 8 grams of

a pale yellow oil which had an agreeable, camphor-like odour, and solidified on cooling; the product, when treated with a small quantity of light petroleum and drained on earthenware, weighed 6 grams.

The *α-oxime*, obtained in this manner, was crystallised from boiling light petroleum, then from dilute alcohol, and recrystallised from light petroleum, forming clusters of transparent plates which melt at 178°.

0·2050 gave 0·5019 CO_2 and 0·1770 H_2O. C = 66·77; H = 9·60.
0·2063 ,, 13·0 c.c. of nitrogen at 19° and 766 mm. N = 7·30.
$C_{11}H_{19}O_2N$ requires C = 67·00; H = 9·64; N = 7·10 per cent.

A solution containing 0·5890 gram dissolved in 25 c.c. of chloroform gave α_D 3°58′ in a 2-dcm. tube, whence $[\alpha]_D$ 84·2°; in the course of 24 hours this rotation fell to α_D 3°7′ corresponding to $[\alpha]_D$ 66·1°, and on allowing the solution to evaporate spontaneously, and recrystallising the residue from light petroleum, it was found to consist entirely of the γ-oxime (see below).

The α-oxime dissolves readily in 10 per cent. potassium hydroxide, forming a colourless solution which remains clear when boiled and does not yield a characteristic precipitate with ferrous sulphate; potassium permanganate is reduced at once to manganate, and potassium ferricyanide also oxidises the substance immediately, yielding a colourless, flocculent precipitate. A solution in 10 per cent. sulphuric acid does not change at common temperatures, and the unaltered oxime is precipitated on dilution or neutralisation with sodium carbonate, but if the liquid is boiled, the oxime is converted into the anhydride.

The two compounds isomeric with the foregoing substance were found in the 25 per cent. solution of potassium hydroxide with which the ether was extracted. This liquid was acidified with glacial acetic acid, which furnished a colourless, crystalline precipitate, and it is necessary to mention that as the alkaline liquid becomes turbid on warming, acidification must be conducted without removing the dissolved ether. Eight grams of the mixed oximes were obtained, and by fractional extraction with boiling light petroleum indefinite nodules were separated from less readily soluble needles.

The *β-oxime*, the more soluble of these two compounds, dissolves freely in boiling light petroleum, and melts at 183°.

0·1519 gave 0·3717 CO_2 and 0·1310 H_2O. C = 66·73; H = 9·58.
0·1312 ,, 8·0 c.c. of nitrogen at 18° and 763 mm. N = 7·07.
$C_{11}H_{19}O_2N$ requires C = 67·00; H = 9·64; N = 7·10 per cent.

A solution containing 0·5224 gram in 25 c.c. of chloroform gave α_D 2°50′ in a 2-dcm. tube, whence $[\alpha]_D$ 67·8°; this value, unlike that of the α-oxime, does not change when the solution is exposed to sunlight

during several days, and on allowing the chloroform to evaporate spontaneously, the major portion is recovered unaltered, the small proportion which changes into the γ-oxime being produced, most likely, during the process of crystallisation from hot petroleum.

The substance resembles the α-oxime in the behaviour of its alkaline solutions towards potassium permanganate, potassium ferricyanide, and ferrous sulphate, but differs from it in changing rapidly into the anhydride when a solution in 10 per cent. potassium hydroxide is boiled; it may be recovered unchanged from solutions in 10 per cent. sulphuric acid if these are neutralised promptly with sodium carbonate, but in the course of 1 hour dehydration occurs, and the liquid becomes turbid. If the dry substance is heated on the water bath, it changes into the γ-modification.

The *γ-oxime*, under which reference is made to the sparingly soluble needles associated with the β-oxime removed from ethereal solution by 25 per cent. potassium hydroxide, is insoluble in cold petroleum, 1 gram requiring about 600 c.c. of the hot solvent (b. p. 60—80°), from which it separates in long, silky needles, melting at 187°.

0·1922 gave 0·4739 CO_2 and 0·1644 H_2O. C = 67·24 ; H = 9·52.
0·2102 „ 13·4 c.c. of nitrogen at 16° and 754 mm. N = 7·37.
$C_{11}H_{19}O_2N$ requires C = 67·00 ; H = 9·64 ; N = 7·10 per cent.

A solution containing 0·3240 gram in 25 c.c. of chloroform gave α_D 1°10′ in a 2-dcm. tube, whence $[\alpha]_D$ 45·0°. The substance undergoes no change at 100° during several days, but resembles the isomerides in the behaviour of solutions in 10 per cent. potassium hydroxide towards potassium permanganate, potassium ferricyanide, and ferrous sulphate; it distinguishes itself from the α-oxime, but resembles the β-modification, in yielding the oily anhydride when the solution in alkali is boiled, and the same change occurs readily on warming the solution in 10 per cent. sulphuric acid. Attempts to benzoylate the compound in pyridine and by the Schotten-Baumann process led in each case to a slimy product, probably consisting of the benzoyl derivative associated with the anhydride.

In order to ascertain which of the three oximes is derived from the stable modification of *iso*nitrosocamphor, 20 grams of the latter, prepared by differential oxidation of the mixture with potassium ferricyanide, were treated with magnesium methyl iodide under the conditions first described, when it was found that the γ-oxime alone is produced. Furthermore, an experiment in which 20 grams of the mixed *iso*nitrosocamphors were added to a solution of magnesium methyl iodide prepared from 100 grams of the alkyl halide instead of 50 grams, yielded the β- and γ-oximes alone, from which it appears

that great excess of the magnesium compound is unfavourable to the formation of the α-oxime.

The Oxime Anhydride, $C_8H_{14}<\begin{matrix}C{=\!=}N\\ |\quad\ \ |\\ CMe\cdot O\end{matrix}$.

It has been stated that the α-oxime is distinguished from the isomeric substances by the stability of alkaline solutions, which, in the case of the β- and γ-modifications, rapidly become turbid when heated. Five grams of recrystallised γ-oxime were dissolved in 15 per cent. potassium hydroxide, and warmed on the water-bath during 1 hour; the colourless oil which separated was collected with ether, and after removing the solvent, was allowed to remain 14 days in the desiccator.

0·2167 gave 0·5804 CO_2 and 0·1818 H_2O. C = 73·05; H = 9·32.
0·2934 „ 21·1 c.c. of nitrogen at 19° and 762 mm. N = 8·37.
$C_{11}H_{17}ON$ requires C = 73·74; H = 9·50; N = 7·82 per cent.

A solution containing 0·4150 gram in 20 c.c. of chloroform gave α_D 2°55′ in a 2-dcm. tube, whence $[\alpha]_D$ 70·3°. The anhydride is only very slightly volatile in steam, the vapour having a faint odour of camphor; it does not reduce potassium permanganate after the first few drops have been added.

Conversion of the O-*Methyl Ether of* iso*Nitrosocamphor into Dimethylaminocamphor.*

Thirty grams of the finely divided ether were slowly added to a well-cooled solution of magnesium methyl iodide prepared from 100 grams of the alkyl halide and 15 grams of magnesium. A vigorous action took place, the solid becoming brown and then dissolving; after 12 hours, the liquid was decomposed with ice followed by acetic acid, which precipitated lustrous leaflets. The crystals were filtered, washed with ether, and recrystallised from boiling water, which deposited 14 grams of dimethylaminocamphor acetate in hard, lustrous, prismatic needles, whilst the mother liquor, united with the solution of magnesium acetate, yielded 5 grams of the base on steam distillation after treatment with alkali.

0·1740 gave 0·4718 CO_2 and 0·1702 H_2O. C = 73·94; H = 10·86.
$C_{12}H_{21}ON$ requires C = 73·84; H = 10·77 per cent.

The dimethylaminocamphor liberated from the recrystallised acetate is a colourless oil which crystallises in needles, and boils at 241° under 785 mm. pressure; a solution containing 0·8497 gram in 25 c.c. of

S 2

absolute alcohol gave α_D 3° 24′ in a 2-dcm. tube, whence $[\alpha]_D$ 50·0°. It does not reduce Fehling's solution, and is affected only slowly by ammoniacal silver nitrate. The picrate, which is only moderately soluble in hot alcohol, crystallises in fern-like aggregates, and melts at 220°, when it decomposes; the hydriodide separates from boiling water in inch-long, flat, lustrous needles, which melt and decompose at 251°. The *platinichloride* is very sparingly soluble in boiling alcohol, but dissolves on adding hydrochloric acid, and crystallises in transparent, glittering, orange plates, which melt and decompose at 211°. The *acetate* is a characteristic salt which begins to darken about 210°, and melts, evolving gas, at 251°.

Formation of Dimethylaminocamphor from the Colourless Benzoyl Derivative of iso*Nitrosocamphor.*

Fifteen grams of the colourless benzoyl derivative were added to a well-cooled ethereal solution of magnesium methyl iodide prepared from 50 grams of methyl iodide and 7·2 grams of magnesium, the action being immediate and vigorous. After 12 hours, the product was decomposed with ice, and on adding excess of acetic acid the characteristic acetate of dimethylaminocamphor was precipitated; when recrystallised from boiling water, the product weighed 12 grams, and a further quantity of the base weighing 2 grams was obtained by uniting the mother liquor with the solution of magnesium acetate, adding alkali, and distilling in a current of steam.

Action of Benzenesulphonic Chloride on the syn- *and* anti-*Modifications of* iso*Nitrosocamphor.*

Twenty grams of the *syn*-modification (m. p. 152°) were dissolved in 100 c.c. of pyridine, and treated with 20 grams of benzenesulphonic chloride; the temperature rose, but there was no separation of pyridine hydrochloride. After 4 hours, 200 c.c. of water were added, precipitating an oil which rapidly crystallised, the product being insoluble in alkali, and weighing 16 grams. Recrystallised twice from absolute alcohol and once from ethyl acetate, the substance was obtained in long, lustrous needles melting at 152°.

0·2166 gave 0·5553 CO_2 and 0·1570 H_2O. C = 69·92; H = 8·05.
0·1506 ,, 10·5 c.c. of nitrogen at 18° and 776 mm. N = 8·22.
$C_{20}H_{28}O_3N_2$ requires C = 69·77; H = 8·14; N = 8·14 per cent.

A solution containing 0·2481 gram dissolved in 25 c.c. of chloroform gave α_D 2°48′ in a 2-dcm. tube, whence $[\alpha]_D$ 141·1°. The substance is identical with the colourless anhydride obtained from the *pseudo*-benzoyl derivative and alcoholic ammonia (Trans., 1904, **85**, 907).

On subjecting the *anti*-modification of *iso*nitrosocamphor (m. p. 114°) to the same treatment, a product was obtained which crystallised from alcohol in lustrous, sulphur-yellow needles melting at 195°, and giving $[\alpha]_D$ 139·2° in chloroform; it is therefore identical with the yellow anhydride of *iso*nitrosocamphor obtained by the action of mild dehydrating agents on the alkali derivatives (Trans., 1903, **83**, 530).

1 : 2-*Dimethylcamphanediol*, $C_8H_{14}<\begin{matrix}CMe\cdot OH \\ | \\ CMe\cdot OH\end{matrix}$.

Fifty grams of camphorquinone were added to a solution of magnesium methyl iodide prepared from 28 grams of the metal and 200 grams of methyl iodide in 500 c.c. of absolute ether; the substance was converted immediately into a dark red solid which rapidly dissolved with effervescence, forming a colourless solution. After 12 hours, the magnesium compound was decomposed with ice followed by acetic acid, and the ethereal portion distilled on the water-bath; the residue being yellow, was warmed with an alcoholic solution of hydroxylamine, which rendered it colourless, and was then submitted to a current of steam, yielding 44 grams of a snow-white, volatile solid. This product was crystallised from light petroleum, which dissolves it readily when warm, and deposits magnificent transparent prisms melting at 132°.

0·1685 gave 0·4470 CO_2 and 0·1670 H_2O. C = 72·35; H = 11·01.
$C_{12}H_{22}O_2$ requires C = 72·72; H = 11·11 per cent.

In dilute solutions the glycol appears to be optically inactive, but 3·0673 grams dissolved in 25 c.c. of absolute alcohol gave α_D 14′ in a 2-dcm. tube, whence $[\alpha]_D$ 0·95°.

At first it was hoped that by replacing the hydroxyl groups with chlorine or bromine, and reducing the halogen derivative thus obtained, it would be possible to prepare the hydrocarbon dimethylcamphane, but the glycol is so sensitive to dehydrating agents that very little can be done with it. Sulphuric acid, hydrobromic acid, phosphorus pentachloride, and acetic anhydride convert it into indefinite oils; phenylcarbimide has no action on it, but calcium chloride yields an amorphous, solid derivative which is not hygroscopic, and which regenerates the glycol when treated with boiling water.

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XXIX.—*The Estimation of Saccharin.*

By Charles Proctor, F.I.C.

For the estimation of the very small quantities of saccharin used for sweetening aërated waters, and other articles of food and drink, the process generally followed has been to extract the saccharin with ether or other solvent, and then to fuse the residues obtained in silver crucibles either with pure caustic potash and potassium nitrate or with pure caustic soda.

In the former case, the sulphur of the saccharin and other associated sulphamido-compounds is oxidised to sulphate and can be estimated as barium sulphate. By this method, no distinction is drawn between real saccharin (*o*-benzoic sulphinide) and *p*-sulphamidobenzoic acid; but where this is not necessary the results are fairly satisfactory, and the method has the advantage of giving a weighable quantity of barium sulphate from a very small quantity of commercial saccharin.

By fusion with caustic soda under suitable conditions real saccharin (*o*-benzoic sulphinide) is transformed into sodium salicylate, which can be detected and estimated by the coloration given by an iron salt in neutral or faintly acid solutions. The salicylic acid test is very delicate and is capable of detecting minute quantities of saccharin. There appears to be little doubt, however, that some wines and fruits yield more or less salicylic acid when their ethereal extract is fused with caustic soda, and as a qualitative test the salicylic acid method must be used with some caution.

The transformation of real saccharin into salicylic acid appears to be a fairly quantitative reaction under suitable conditions; and, as *p*-sulphamidobenzoic acid, or other impurities likely to be present in commercial saccharin, do not yield salicylic acid, this method can be employed for estimating the percentages of real saccharin in commercial samples.

Satisfactory results, however, can only be obtained when standard samples of pure *o*-benzoic sulphinide are fused at the same time and otherwise treated in exactly the same manner as the samples under examination. Apparently very slight variations at any stage of the experiment will cause somewhat wide differences in the results, and rigorous attention to every detail is therefore necessary. There is also always some difficulty in exactly matching the colorations produced by the iron salt; and, where the percentages of pure saccharin in the samples under examination differ widely from the standard, the dilutions necessary to obtain correspondence in the tints may give rise to rather large experimental errors.

When applied to the ordinary commercial saccharins, or to mixtures of saccharin with alkali carbonates which can be directly fused with caustic soda, the salicylic acid method, except for the somewhat close attention to details required, is a comparatively simple process. But when the saccharin is mixed with other substances, it is usually necessary to extract it with ether or other solvent, and the residues may have to be purified from colouring matter and separated from salicylic acid before the fusion with caustic soda. This is often very troublesome, and sometimes practically impossible. When applied to the mixtures and residues from saccharin factories, for instance, the results obtained were unsatisfactory, probably owing to the presence of *o*-toluenesulphonamide, and possibly other ortho-compounds, which on fusion with caustic soda yield some salicylic acid. These substances cannot be readily separated from the saccharin, and any process for estimating saccharin which would enable these preliminary extractions and purifications to be dispensed with would be a great convenience.

A process of this kind has been described, the principle of which appears to be due to Remsen and Burton, who, in 1890 (*Amer. Chem. J.*, **11**, 403—408), showed that when commercial saccharin was boiled with dilute hydrochloric acid for about an hour, the ortho-compound was changed into the acid ammonium salt of sulphobenzoic acid, whilst *p*-sulphamidobenzoic acid remained unaltered. They described a method of estimating the two substances by concentrating the hydrolysed solution, cooling, and allowing the *p*-sulphamidobenzoic acid to crystallise, the crystals being then filtered off, washed, dried, and weighed.

In 1894, Hefelmann (*Pharm. Centr. Blatt*, **35**, 105) described a somewhat similar method, using 71 per cent. sulphuric acid as the hydrolysing agent, but finally treating the solution with excess of caustic soda, distilling off and estimating the ammonia produced as in the Kjeldahl process for estimating nitrogen.

Some years later, E. Emmet Reid (*Amer. Chem. J.*, 1899, **21**, 461) made a series of analyses of pure saccharin (*o*-benzoic sulphinide), of pure *p*-sulphamidobenzoic acid, and of commercial samples of saccharin by Hefelmann's process. As a result of his experiments, Reid came to the conclusion that the percentage of pure saccharin in commercial samples could be accurately determined by estimating the ammonia produced on hydrolysis in the manner described by Hefelmann, but he found that dilute hydrochloric acid, as suggested by Remsen and Burton, was a more satisfactory and convenient hydrolysing reagent than the comparatively strong sulphuric acid used by Hefelmann.

I have recently tested Emmet Reid's process in the analysis of

a number of commercial saccharins, salts of saccharin, and mixtures containing saccharin, as well as the intermediate products and solutions obtained in the manufacture of saccharin. My experiments show that the process is reliable, and that the results obtained are not likely to be affected by any of the by-products present in commercial saccharins, or by the mineral salts and solutions with which such saccharins are usually mixed.

The process is carried out as follows: 0·5 to 1 gram of the saccharin or saccharin mixture is weighed into a glass flask of 100—120 c.c. capacity, and 50 c.c. of approximately normal hydrochloric acid are added. The flask, fitted with an air-condenser, is gently boiled on a sand-bath, or over a small bunsen flame, for two and a half hours, the ammonia produced being subsequently estimated by the ordinary Kjeldahl process, when the number of c.c. of $N/10$ sulphuric acid neutralised by the ammonia multiplied by 0·0183 gives the weight of pure saccharin (*o*-benzoic sulphinide) in grams.

The following are examples of the results obtained in our experiments:—

No. of sample.	Sample.	Weight taken.	$N/10$ H_2SO_4 neutralised by ammonia.	Equivalent weight of saccharin.	Percentage.
		Gram.	c.c.	Gram.	
1	"Pure" saccharin	0·700	37·5	0·6863	98·0 }
		0·700	37·4	0·6844	97·8 }
		0·500	26·6	0·4868	97·4
2	"Pure" saccharin	0·500	27·2	0·4978	99·5 }
		0·500	27·1	0·4959	99·2 }
3	"Pure" saccharin	0·500	24·1	0·4410	88·2 }
		0·500	24·2	0·4428	88·5 }
4	Commercial saccharin (60 per cent.)	0·500	17·0	0·3111	62·2 }
		0·500	16·9	0·3093	61·8 }
5	Anhydrous sodium salts of saccharin (90 per cent.)	0·500	24·4	0·4465	89·3
6	"Sucramine" (ammonium salt)	0·700	69·6		
	Less direct		34·8*		
			34·8	0·6368	90·9
7	Saccharin tablets (A)	0·9522	19·8	0·3624	38·1 }
		0·9422	20·0	0·3660	38·8 }

* Ammonia derived from the salt.

No. of sample.	Sample.	Weight taken.	$N/10$ H_2SO_4 neutralised by ammonia.	Equivalent weight of saccharin.	Percentage.
		Gram.	c.c.	Gram.	
8	Saccharin tablets (B)........	1·1250 1·1282	22·5 22·5	0·4118 0·4118	36·6 36·5
9	Pure "para-saccharin" (*p*-sulphamidobenzoic acid)	0·700 0·700 0·500	nil 0·1 nil	— 0·0018 —	— 0·2 —
10	Mixture of "pure" saccharin from (1) .. . . and pure para-saccharin from (9)...	0·40* 0·30 0·70	21·2	0·3880	55·4
11	Mixture of "pure" saccharin from (1)......................... .... and pure para-saccharin from (9)...	0·65† 0·05 0·70	34·9	0·6386	91·2
12	Pure *o*-toluenesulphonamide......... (made in laboratory)	0·700 0·500	nil nil	— —	— —
13	Commercial *o*-toluenesulphonamide (made in factory)	1·000 0·500	nil nil	— —	— —
14	Recovered *o*-toluenesulphonamide (from factory)	0·500	nil	—	—
15	Recovered *o*-toluenesulphonamide (from factory)	0·500	nil	—	—
16	Recovered *o*-toluenesulphonamide (from factory)	0·500	0·2	0·0037	0·7

* 0·392 gram pure saccharin present.
† 0·637 gram pure saccharin present.

Direct Method.

During the preceding experiments, it was observed that saccharin liberated iodine from a solution containing potassium iodide and iodate. On further investigation, it was found that this reaction was quantitative, and that the *p*-sulphamidobenzoic acid, but not the sulphonamides, also acted in a similar way, although not so readily.

This reaction affords an easy and rapid method of estimating the total percentage of saccharin in commercial samples; and, in

combination with the process already described, it enables one to estimate separately the percentages of the real saccharin (*o*-benzoic sulphinide) of the para-compound (*p*-sulphamidobenzoic acid), and indirectly of the sulphonamides or other non-acid organic compounds which may be present in commercial saccharin or mixtures containing saccharin, or in the intermediate products and residues obtained during the manufacture of saccharin.

The process is carried out as follows:

(*a*) *In Commercial Saccharins*, that is, powders known to consist only of the uncombined ortho-saccharin, with or without admixture of *p*-sulphamidobenzoic acid and traces of sulphonamides.

The powder (0·5 to 1·0 gram) is weighed into a flask of 150 to 200 c.c. capacity, having a well-fitting ground-glass stopper, and 50 to 75 c.c. of recently boiled distilled water are added. Into the mixture a crystal or two of potassium iodide are dropped, and then 10 c.c. of a 5 per cent. solution of potassium iodate, and the whole shaken gently. The pure ortho-saccharin dissolves almost immediately, liberating an equivalent quantity of iodine, which can be titrated with $N/10$ sodium thiosulphate and starch in the usual way. If there is any large proportion of the para-compound present, the powder dissolves much more slowly; and if at the end of five minutes any undissolved powder still remains, before titration, the flask is vigorously shaken once or twice during 15—20 minutes until the solution of the saccharin appears to be complete.

The number of c.c. of $N/10$ sodium thiosulphate required multiplied by 0·0183 expresses the result as grams of real saccharin; and, where it is evident from the progress of the experiment that the admixture of the para-compound is small, the quantity so found will be a close approximation to the combined weight of the ortho- and para-saccharins present in the sample. To obtain the exact proportion of each substance, the ammonia produced on boiling with dilute hydrochloric acid must also be determined as already described, and from the total number of c.c. of $N/10$ thiosulphate required by the iodine liberated in the direct titration of the powder, the number of c.c. of $N/10$ acid required to neutralise the ammonia produced from an equal weight of the powder is subtracted. The difference multiplied by 0·0201 will give the weight in grams of the *p*-sulphamidobenzoic acid in the sample. Thus a sample of "pure" saccharin and three samples of "commercial" saccharin gave the following results:

	1.	2.	3.	4.	5.	Percentage.			
Weight of powder taken.	N/10 thiosulphate required for iodine liberated.	N/10 sulphuric acid required for ammonia produced.	Difference = (1) – (2).	Weight of real saccharin = (2) × 0·0183.	Weight of *p*-sulphamidobenzoic acid = (3) × 0·0201.	Real saccharin.	*p*-Sulphamidobenzoic acid.	Together.	As commercial saccharin from (1) × 0·0183.
Gram	c.c.	c.c.	c.c.	Gram	Gram				
0·500	27·0	26·8	0·2	0·4904	0·0040	98·08	0·80	98·88	98·82
0·500	25·7	24·0	1·7	0·4392	0·0342	87·84	6·84	94·68	94·06
0·500	26·5	24·0	2·5	0·4392	0·0502	87·84	10·04	97·88	96·99
0·500	26·0	24·1	1·9	0·4410	0·0382	88·20	7·64	95·84	95·16

It will be observed that the percentage of "commercial saccharin"—that is, of the mixture of *o*-benzoic sulphinide and *p*-sulphamidobenzoic acid—calculated from the iodine directly liberated does not differ very much from the total percentage of the two compounds actually present, being less than 1 per cent. too low even when the para-compound is present to the extent of 10 per cent. in the mixture.

(*b*) *Where the sample is mixed with sodium carbonate or other alkali carbonates, or where it is in the form of the ammonium or sodium salt of saccharin.*

In this case, 0·5 to 1·0 gram of the powdered sample is weighed in a platinum capsule and covered with about 5 c.c. of pure concentrated hydrochloric acid. The capsule is heated on the steam-bath until the excess of acid has been completely driven off, and then dried for about two hours in the oven.

The residue is washed into a flask, mixed with potassium iodide and iodate, and titrated as before. When treated in this way, the results tabulated on p. 248 were obtained.

On heating with the concentrated hydrochloric acid, the ortho-saccharin is slightly changed to the acid ammonium salt of sulphobenzoic acid, but this does not affect the results, as this salt itself liberates an equivalent quantity of iodine.

When the saccharin is in solution, a quantity, equivalent to between 0·5 and 1·0 gram, can be weighed into a platinum capsule and evaporated with an excess of pure hydrochloric acid, or the saccharin, &c., may be first extracted with ether or other solvent and the residues treated as before.

It is often more convenient, however, to hydrolyse the saccharin by Emmet Reid's process; and then, before distilling off the ammonia, to concentrate and cool the acid solution in an ice-bath.

Sample.		1.	2.	3.	4.	5.	6.	Percentage of		
					Weight of					
Kind.	Weight.	$N/10$-Thiosulphate required for iodine liberated.	$N/10$-Acid required for ammonia produced.	Difference = (1) − (2).	Real saccharin = (2) × 0·0183.	*p*-Sulphamidobenzoic acid = (3) × 0·0201.	Total weight of (4) and (5).	Real saccharin.	*p*-Sulphamido-benzoic acid.	Both substances.
	Grams	c.c.	c.c.	Grms	Gram	Gram	Gram			
Tablets A	0·950	32·9	20·0	12·9	0·3660	0·2593	0·6253 *	38·52	27·30	65·82
Tablets B	1·125	36·6	22·5	14·1	0·4118	0·2834	0·6952 *	36·60	25·19	61·79
Saccharin sodium salt (80 per cent.).....	1·000	44·9	42·4	2·5	0·7759	0·0502	0·8261	77·59	5·02	82·61
"Sucramine" ammonium salt	1·000	49·8	49·7	0·1	0·9095	0·0020	0·9115	90·95	0·20	91·15

* The tablets consist of a mixture of sodium hydrogen carbonate with commercial saccharin (60 parts ortho- and 40 parts para-saccharin).

From the well-cooled solution, the para-compound, together with any sulphonamides, &c., can be easily extracted on shaking up two or three times with about an equal volume of ether. The ether is evaporated off and the residue weighed in a tared flask. To this residue is then added potassium iodide and iodate, and the liberated iodine titrated and calculated as *p*-sulphamidobenzoic acid. The difference between the total weight of the ether residue and that of the para-compound, as thus determined, represents the unaltered sulphonamides, &c. The details of the process may be modified in various ways to suit the necessities of the case in the particular sample under examination, and the extent of the information required from the analysis. Where small percentages of saccharin are present, or only small quantities of the samples are available, more dilute standard solutions—$N/20$ or $N/50$ instead of $N/10$—can be employed. It is always necessary to determine by blank experiments that the reagents and solutions used are free from ammonia, and that the samples contain no ammonium salt; and when dilute solutions are employed, care must be taken to avoid the access of extraneous ammonia.

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XXX.—*The Relation between Natural and Synthetical Glycerylphosphoric Acids.*

By Frederick Belding Power and Frank Tutin.

The fact that glycerylphosphoric acid is a constituent of the molecular complex known as lecithin has led to the medicinal use of a number of salts of this acid and to their chemical study.

The first to prepare glycerylphosphoric acid synthetically was Pelouze (*Compt. rend.*, 1845, **21**, 718, and *J. pr. Chem.*, 1845, **36**, 257), who obtained it by the action of phosphoric oxide or of metaphosphoric acid on glycerol. The analyses recorded by Pelouze of its calcium, barium, and lead salts indicate that under the conditions employed by him a monoglyceryl ester, $C_3H_5(OH)_2{\cdot}O{\cdot}PO(OH)_2$, was obtained, and his purpose in preparing this was to confirm the correctness of the formula previously assigned to glycerol. At about the same time, Gobley had obtained glycerylphosphoric acid from the yolk of egg, and it was stated by Pelouze (*loc. cit.*), solely from analytical comparisons, that not the slightest doubt could be entertained respecting the absolute identity of the glycerylphosphoric acid from this source with that obtained by the action of phosphoric acid on glycerol.

By the interaction of glycerol and phosphoric acid, there is the possibility that several esters may be formed, and the product would therefore contain one or more of these, according to the relative proportions of the interacting substances and to the varying conditions of time, temperature, and pressure to which the mixture is subjected. The only known products of this action, however, appear to be (1) the mono-ester, glycerylphosphoric acid, $C_3H_5(OH)_2{\cdot}O{\cdot}PO(OH)_2$; (2) the so-called di-ester, $C_3H_5(OH){<}^{O}_{O}{>}PO{\cdot}OH$, and (3) the tri-ester or glyceryl phosphate, $C_3H_5{:}PO_4$.

The conditions under which these three esters respectively are formed, and the relative proportions in which they are contained in

the product of the reaction, have been determined by Carré (*Compt. rend.*, 1903, **137**, 1070). He has also shown that by the method usually employed for the preparation of glycerylphosphoric acid it is associated with some of the above-mentioned di-ester, to which the constitution $PO \begin{cases} O—CH_2 \\ OH \quad CH{\cdot}OH \\ O—CH_2 \end{cases}$ has been assigned, and not with the diglycerylphosphoric acid, $[C_3H_5(OH)_2O]_2{:}PO{\cdot}OH$, as had been assumed by Adrian and Trillat (*J. Pharm.*, 1898, **7**, 226).

The discrepancies of statement respecting the composition and characters of the salts of glycerylphosphoric acid (compare Portes and Prunier, *J. Pharm.*, 1894, **29**, 393, and Petit and Polonowsky, *ibid.*, 1894, **30**, 193) are evidently due, as suggested by Carré (*loc. cit.*), to their contamination with the salts of the di-ester. It was therefore deemed of interest to ascertain the characters of the above-mentioned salts when prepared under such conditions as are known to exclude the formation of the di-ester.

In the course of our work, a paper has appeared by Willstätter and Lüdecke (*Ber.*, 1904, **37**, 3753) on the subject of lecithin, in which the relation between the glycerylphosphoric acid obtained from the latter and that prepared synthetically is considered. They claim to have found essential differences between the barium and calcium salts of these two acids, not only with respect to solubility, but especially in the composition of the preparations when dried by heat. Although the salts of the natural acid are lævorotatory, from which they infer that this must have the unsymmetrical formula $\begin{matrix} CH_2{\cdot}O{\cdot}PO_3H_2 \\ CH{\cdot}OH \\ CH_2{\cdot}OH \end{matrix}$, they think there is very little probability that the differences are simply those which usually exist between optically active compounds and the corresponding racemic ones, especially in consideration of the fact that the salts of the glycerylphosphoric acid obtained from lecithin, which served for the purpose of comparison, did not possess their full degree of optical activity, but in the course of preparation had become partially racemised. As an example of these differences, they note that the calcium salt of the partially racemised natural acid, dried at 130°, is anhydrous, whilst that of the synthetical acid prepared by them, on account of containing more than 2 per cent. less of calcium, appears to retain at that temperature $1\frac{1}{2}$ molecules of water. From these considerations, they were led to the conclusion that the glycerylphosphoric acid of Pelouze is different from that obtained from lecithin, although the question as to the cause of this difference and that of the constitution of the synthetical acid was left undecided.

In our investigation, it is shown that the above conclusion of Willstätter and Lüdecke is invalid, as it is evident that the conditions under which they prepared their synthetical glycerylphosphoric acid were such as are now known to afford some of the di-ester, $C_3H_5(OH){<}^{O}_{O}{>}PO{\cdot}OH$ (compare Carré, *loc. cit.*). The differences observed by them in the percentages of metal contained in the salts of the natural acid and in those of their synthetical acid do not, therefore, justify their assumption that the latter retained water when heated to the specified temperatures.

Furthermore, the observation of Willstätter and Lüdecke that the glycerylphosphoric acid from lecithin possessed optical activity, although certainly proving the presence of the unsymmetrical acid in the preparation, does not necessarily exclude the possibility that some of the symmetrical acid was also present. Inasmuch as the natural acid has in no instance been prepared from a lecithin which was known to be a pure substance (compare Bergell, *Ber.*, 1900, **33**, 2584), no proof can as yet be adduced that it is not a mixture of the unsymmetrical and the symmetrical isomerides. The same possibility naturally exists with respect to the homogeneity of the synthetical acid, which, however, doubtless consists chiefly of the unsymmetrical isomeride.

We shall endeavour to prepare both these isomerides in order to compare them, on the one hand with the completely racemised natural acid, and on the other hand with the acid obtained by the interaction of phosphoric acid and glycerol.

Experimental.

In order to determine and compare the characters of some of the salts of glycerylphosphoric acid, when prepared by definite methods, the following experiments were conducted.

I. Twenty-five grams of glycerol and 30 grams of phosphoric acid (sp. gr. 1·70) were mixed, and heated together for 24 hours (in three periods of 8 hours each), in an oil-bath at 105—110°. The mixture was then added to an excess of milk of lime, the liquid filtered when cold, and the precipitate thoroughly washed with water. The combined filtrate and washings, after being deprived of the excess of lime by means of carbon dioxide, were divided into two portions, (*a*) and (*b*), which were evaporated to a small bulk, when some of the salt separated.

(*a*) In one case, the calcium salt which had separated from the hot liquid was collected, and washed with a little hot water.

1·1031 of the salt, dried at 125°, gave 0·2940 CaO. Ca = 19·04 per cent.

(*b*) In the other case, the calcium salt was completely precipitated

by the addition of alcohol. This was collected and washed with alcohol.

1·0100 of the salt, dried at 125°, gave 0·2695 CaO. Ca = 19·06.

$C_3H_7O_6PCa$ requires Ca = 19·04 per cent.

II. A mixture of glycerol and phosphoric acid, in the above-mentioned proportions, was heated for the same length of time as in I, but at 120—125°. The calcium salt was obtained by complete precipitation with alcohol.

1·0245 of the salt, dried at 125°, gave 0·2464 CaO. Ca = 17·2 per cent.

III. A mixture of glycerol and phosphoric acid was heated in the same proportions and for the same length of time as in the preceding experiments, but at 135°. The calcium salt was obtained by complete precipitation with alcohol.

1·0512 of the salt, dried at 125°, gave 0·2466 CaO. Ca = 16·7 per cent.

It is evident from the above results that when glycerylphosphoric acid is prepared at temperatures above 110° it is associated with varying amounts of the di-ester, the calcium salt of which requires Ca = 11·56 per cent.

Having confirmed the conditions, ascertained by Carré (*loc. cit.*), under which only the mono-ester (I) is formed, a considerable quantity of it was prepared for the purpose of examining some of its salts more completely.

Calcium Glycerylphosphate, $O=P\begin{cases}O\cdot C_3H_5(OH)_2\\ O\rangle Ca\\ O\end{cases}$.

This salt forms tufts of crystalline leaflets when its cold, saturated solution is heated on a water-bath; it is soluble at 16° in 22·4 parts, at 25° in 25·2 parts, and at 100° in 108·6 parts of water; it is insoluble in alcohol.

0·5696, previously dried in a vacuum, lost on heating at 125° 0·0044 or 0·77 per cent. This salt was therefore practically anhydrous, since half a molecule of water would require a loss of 4·1 per cent.

0·5652, dried at 125° gave 0·1523 CaO. Ca = 19·25.

$C_3H_7O_6PCa$ requires Ca = 19·04 per cent.

0·6954, dried at 125°, gave after ignition, solution in nitric acid, and precipitation by ammonium molybdate, 0·3649 $Mg_2P_2O_7$. P = 14·75.

$C_3H_7O_6PCa$ requires P = 14·76 per cent.

For further confirmation of the composition of this salt, its combustion with both copper oxide and lead chromate was attempted, but

owing to the difficulty of completely burning away the carbon, only the hydrogen was estimated.

0·3651, dried at 125°, gave 0·1129 H_2O. H = 3·43.
0·3907, „ „ „ 0·1191 H_2O. H = 3·38.
$C_3H_7O_6PCa$ requires H = 3·33 per cent.

Strontium Glycerylphosphate, $O{=}P{\leftarrow}\begin{matrix}O{\cdot}C_3H_5(OH)_2 \\ O > Sr \\ O\end{matrix}$.

This salt, like that of calcium, is more sparingly soluble in hot than in cold water. On heating a cold, saturated solution of it on a water-bath, it separated as a white, granular powder.

0·4957, previously dried in a vacuum, lost, on heating at 125°, 0·0074 or 1·49 per cent. Half a molecule of water would require a loss of 3·37 per cent.

0·4883, dried at 125°, gave 0·3451 $SrSO_4$. Sr = 33·7.
$C_3H_7O_6PSr$ requires Sr = 34·0 per cent.

Barium Glycerylphosphate, $O{=}P{\leftarrow}\begin{matrix}O{\cdot}C_3H_5(OH)_2 \\ O > Ba \\ O\end{matrix}$.

This is similar in its properties to the strontium salt.

0·4550, previously dried in a vacuum, lost, on heating at 125°, 0·0041 or 0·90 per cent. Half a molecule of water would require a loss of 2·84 per cent.

0·4401, dried at 125°, gave 0·3301 $BaSO_4$. Ba = 44·1.
$C_3H_7O_6PBa$ requires Ba = 44·7 per cent.

The following salts were all prepared from a solution of the pure barium salt by exact precipitation with a solution of the sulphate of the respective metal, filtering, and concentrating the filtrate.

Lithium Glycerylphosphate, $O{=}P{\leftarrow}\begin{matrix}O{\cdot}C_3H_5(OH)_2 \\ OLi \\ OLi\end{matrix}$.

This salt is very readily soluble in cold, but only moderately so in hot water. On warming its cold, saturated solution, it is deposited in tufts of small leaflets.

0·2934 of the air-dried salt, heated at 125°, lost 0·0204 or 6·9 per cent.

This represents between one-half and one molecule of water, which would require respectively a loss of 4·6 and 8·9 per cent.

0·3842 of the anhydrous salt gave, on ignition, 0·2101 $Li_4P_2O_7$. $Li_4P_2O_7 = 54·6$.

$C_3H_7O_6PLi_2$ requires $Li_4P_2O_7 = 54·9$ per cent.

0·2703 of the anhydrous salt gave, after ignition and solution in water, 0·1634 $Mg_2P_2O_7$. P = 16·8.

$C_3H_7O_6PLi_2$ requires P = 16·7 per cent.

The *sodium* salt was first obtained as a syrup, but on remaining for several weeks in a vacuum over sulphuric acid, glistening leaflets slowly formed. The analysis of this salt indicated that it was not perfectly pure, and the amount was too small to admit of its recrystallisation.

The *potassium* salt was only obtained in the form of an uncrystallisable syrup.

The *ammonium* salt, on concentrating its solution, likewise formed a syrup, and, when this was allowed to remain in a vacuum over sulphuric acid, it gradually dissociated, with the loss of ammonia.

Manganese Glycerylphosphate, $O = P \begin{cases} O \cdot C_3H_5(OH)_2, 3H_2O \\ O \\ O \end{cases} \!\!> Mn$.

This salt is moderately soluble in cold, but very sparingly so in hot water. On warming its cold solution, it separates in tufts of small, well-defined needles of a light pink colour.

0·4617 of the air-dried salt, heated at 125°, lost 0·0873 H_2O. $H_2O = 18·9$.

$C_3H_7O_6PMn,3H_2O$ requires $H_2O = 19·3$ per cent.

0·3744 of the anhydrous salt gave 0·1255 Mn_3O_4. Mn = 24·1.

$C_3H_7O_6PMn$ requires Mn = 24·4 per cent.

Zinc Glycerylphosphate, $O = P \begin{cases} O \cdot C_3H_5(OH)_2, \frac{1}{2}H_2O \\ O \\ O \end{cases} \!\!> Zn$.

This salt, unlike most of the other salts of glycerylphosphoric acid, is more readily soluble in hot than in cold water. It also crystallised with greater facility than any of the preceding salts, and on cooling its hot concentrated solution separated as a mass of colourless, glistening plates. On heating at 125°, it underwent some change, apparently becoming converted into a basic salt, which was insoluble in water.

0·3769 of the air-dried salt gave 0·1221 ZnO. Zn = 26·0.

$C_3H_7O_6PZn,\frac{1}{2}H_2O$ requires Zn = 26·7 per cent.

Examination of the Salts of Glycerylphosphoric Acid prepared by Willstätter and Lüdecke's Method.

In order to test the validity of the conclusions of Willstätter and Lüdecke (*Ber.*, 1904, **37**, 3753) respecting the difference which they supposed to exist between the natural and synthetical glycerylphosphoric acids, we have also prepared some of the barium and calcium salts of the latter acid exactly in accordance with the method adopted by them. From the results of our initial experiments (II and III), it was to be expected that the salts obtained by the method of the above-mentioned investigators would not consist wholly of those of the mono-ester, but would contain varying amounts of the corresponding salts of the di-ester, a fact which they appear to have completely overlooked, and which is rendered evident by a consideration of the analytical data.

Molecular proportions of crystallised phosphoric acid and pure dry glycerol (53·2 grams of the former and 50 grams of the latter) were heated together in an oil-bath at 135—140° under 15 mm. pressure, and the water eliminated by the reaction absorbed by strong sulphuric acid contained in a flask adapted to the apparatus. After 6 hours, acrolein was given off, and the heating was then discontinued. The mixture was poured into an excess of baryta solution, and, when cold, the liquid was filtered, and the precipitate thoroughly washed with water. The combined filtrate and washings, after being freed from baryta by carbon dioxide, was again filtered, and concentrated on a water-bath to a small bulk. The salt was then completely precipitated by the addition of alcohol, collected on a filter, washed with alcohol, and dried in the air.

Barium Salt.—A portion of this salt was dissolved in water, the solution filtered, concentrated, precipitated by alcohol, and these operations repeated five times consecutively. This product was then dissolved in water and the salt which separated by heating the solution on a water-bath was collected and analysed.

0·4322, dried at 105° until of constant weight, gave 0·3176 $BaSO_4$. Ba = 43·2 per cent.

Another portion of the barium salt was precipitated from its aqueous solution six times successively by alcohol, and was then analysed without subsequent treatment with water.

0·3040, dried at 105° until of constant weight, gave 0·2139 $BaSO_4$. Ba = 41·4 per cent.

As a barium salt of the mono-ester requires Ba = 44·6 per cent., Willstätter and Lüdecke (*loc. cit.*), having found a somewhat lower

percentage of barium, calculate their results for a salt having the composition $C_3H_7O_6PBa,H_2O$, but without any direct evidence that it contained a molecule of water. They also consider it remarkable that the salt precipitated by alcohol contains relatively less barium than that obtained by heating the aqueous solution. As we have previously shown, however, the lower percentage of barium in these salts is not due in either case to the presence of water, but to a salt of the di-ester, and this is in relatively greater proportion when the salt is precipitated by alcohol than when separated by heating the aqueous solution.

Calcium Salt.—This was prepared from the original barium salt, obtained by the above-described method, by shaking its solution with freshly precipitated calcium sulphate until the liquid no longer gave a reaction for barium. The filtered liquid was then concentrated on a water-bath, and the salt which separated from the hot solution was collected. It was first dried in a vacuum over sulphuric acid until of constant weight, and then analysed.

0·6435, heated at 125—130°, lost 0·0262 H_2O. $H_2O = 4·07$.
0·6191, „ 125—130°, gave 0·1447 CaO. Ca = 16·69 per cent.

Willstätter and Lüdecke, in interpreting the results of their analysis of this salt, state that the loss of weight on heating at 125—130° appears to correspond to $\frac{3}{4}$ molecule of water, and that when heated at this temperature it contains an amount of calcium (16·69 per cent.) agreeing best with the formula $C_3H_7O_6PCa,1\frac{1}{2}H_2O$, which requires Ca = 16·87 per cent.

It should be considered, however, that as anhydrous calcium glycerylphosphate contains 19·04 per cent., and the corresponding salt of the di-ester 11·56 per cent. of calcium, a mixture of these two salts in the proportion of 69 per cent. of the former and 31 per cent. of the latter would contain 16·72 per cent. of calcium, or almost precisely the amount that was found in the salt assumed to contain $1\frac{1}{2}$ molecules of water. It has been found possible to decide which of these conditions obtains by estimating the total amount of hydrogen in the salt. This was accomplished by its combustion with copper oxide, as indicated in the case of the previously described calcium salt.

0·3715, previously heated at 125—130°, gave 0·1121 H_2O. H = 3·35.
0·3742, „ „ „ „ 0·1167 H_2O. H = 3·46.
per cent.

A mixture, in the above-mentioned proportions, of the calcium salts of the two esters requires H = 3·37 per cent., whereas a salt of the mono-ester with $1\frac{1}{2}$ molecules of water requires H = 4·22 per cent.

It is evident, therefore, that the salt obtained under the conditions employed by Willstätter and Lüdecke was a mixture of the calcium salts of the mono- and di-esters, and not the hydrated salt of the mono-ester, as they have assumed. This conclusion is, furthermore, supported by the results obtained by Carré (*loc. cit.*) in his investigation of the products of the interaction of glycerol and phosphoric acid under varying conditions of temperature and pressure.

Moreover, it has been shown that it is possible under certain conditions to obtain a synthetical glycerylphosphoric acid, the salts of which agree with those of a mono-ester, and, on comparing the barium and calcium salts of this synthetical acid with those prepared by Willstätter and Lüdecke from the glycerylphosphoric acid from lecithin, the only apparent difference in composition is in the amount of water retained by the calcium salt after drying in a vacuum.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
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XXXI.—*The Formation of Magnesia from Magnesium Carbonate by Heat, and the Effect of Temperature on the Properties of the Product.*

By WILLIAM CARRICK ANDERSON.

MAGNESIUM oxide prepared by different methods is known to be subject to wide variations in properties. That obtained by gentle heating of the native carbonate reacts quickly with water, and, when in presence of a limited amount of water, "sets" to a firm mass. The product obtained by heating similarly the artificial carbonates does not "set," although it also appears to slake rapidly with water, but if these carbonates be treated with nitric acid and the resulting nitrate ignited gently, the oxide left will "set" similarly to that obtained from the native carbonate by heat. Again, when magnesite is heated not to a moderate temperature, but to a white heat, the residue remains practically unacted on by water even after the lapse of a considerable time. The specific gravities of the oxides obtained by these methods are also different, as can be appreciated by a glance at the relative bulks they occupy.

In the following investigation, an endeavour was made to ascertain (1) the temperature at which the carbonates of magnesium are fully decomposed into oxide in the open air; (2) the effect produced on some selected property of the oxide by maintaining it at a definite tempera-

ture for a known period after its formation; and (3) whether the resulting changes took place gradually or *per saltum* as the limit of temperature was raised.

The property selected for examination in (2) and (3) was the relative solubility in water or the amount of magnesia dissolved in 2 hours by 200 c.c. of distilled water at 20° from a large excess of the oxide. Approximately the same amount of magnesia by weight was used in each experiment.

Regarding the actual solubility of magnesia in water, very little information is to be found in the literature, and for the purpose of this investigation it was not considered essential to fix this exactly. The researches bearing on the point are for the most part of earlier date, and even in the later ones there is usually no description of the preliminary treatment to which the oxide has been exposed. Fyfe (*Edinburgh Phil. J.*, 1821, **5**, 305) quotes Henry to the effect that water does not dissolve more than 1/2000th part of its weight of magnesia (say 500 milligrams per litre), while Kirwan gives its solubility as 1 in 7900 parts of water (126·6 milligrams per litre). Dalton's number, quoted by the same authority, is 1 part in 16,000 at the ordinary temperature, or 62·5 milligrams per litre. Fresenius (*Annalen*, 1846, **59**, 117) states that 1 part of magnesia dissolves in 55,368 parts of cold or hot water, this being equivalent to 18·06 milligrams per litre; Bunsen gives 1 part in 100,000—200,000, and Bineau (*Compt. rend.*, 1855, **41**, 510) 1 part in 50,000—100,000. Fyfe (*loc. cit.*) states that he obtained the magnesia used in his experiments on solubility by precipitating the sulphate by an alkaline basic carbonate, washing the precipitate until the filtrate gave no reaction with barium nitrate, and finally exposing the residue to a red heat until all the carbon dioxide was expelled. He estimated the dissolved magnesia by precipitation with ammonium carbonate and sodium phosphate, and thus found that 1 part of magnesia dissolved in 5142 parts of water at the ordinary temperature (194·5 milligrams per litre). At the boiling point, the solubility was found to be 1 part in 36,000 of water. A determination has been made more recently by Kohlrausch and Rose (*Zeit. physikal. Chem.*, 1893, **12**, 241), who calculate from the electrical conductivity of the solution that 1 litre of water dissolves 9 milligrams of $Mg(OH)_2$ (6·2 milligrams of the oxide per litre).

Experimental.

The samples of magnesia employed in the experiments described below were prepared by heating the carbonates in a Heraeus electric resistance-furnace of the horizontal type. The tube of the furnace

was closed at either end by a thick sheet of asbestos, and the temperature record was obtained by means of a platinum-rhodium thermocouple connected to a Siemens and Halske galvanometer. The instrument was standardised at the Physikalisch-technische Reichsanstalt, Berlin. The forms of carbonate used were a very pure magnesite from Eubœa, which, however, could not be obtained entirely free from calcium, and the purest artificial preparations sold by Merck as "heavy," "light," and "crystal" magnesium carbonates, and were found to contain only small traces of alkali carbonate. These substances were all finely ground and heated in an open platinum boat or capsule, 1 gram being used in each experiment.

Decomposition of Magnesium Carbonate by Heat.—Experiments were first made in order to ascertain the lowest temperature at which the evolution of carbon dioxide from these carbonates could be recognised when they were heated under atmospheric pressure. A very slow current of air was passed over the heated sample, and was then caused to bubble through a clear solution of baryta water in a closed vessel. This develops a greasy-looking film on its surface when a trace of carbon dioxide comes into contact with it, before the granular precipitate of the carbonate makes its appearance. The lowest temperatures at which, in experiments of 20 minutes' duration, the films were distinctly recognisable were as follows:

Magnesite	405°	"Light" carbonate ...	352°
"Heavy" carbonate ...	368	"Crystal" ,, ...	271·5

To determine more exactly the rate at which the carbon dioxide was evolved at these low temperatures, samples of the ground magnesite were heated for 20 hours in a slow current of dry air and the carbon dioxide estimated directly by absorption in caustic potash, and indirectly by ascertaining the loss the sample had undergone in weight. The magnesite used contained only 0·2 per cent. of moisture. The maximum variation of temperature recorded was about 3°.

I.			II.		
Temperature.	Period of heating.	Loss of CO_2 from 1 gram.	Temperature.	Period of heating.	Loss of CO_2 from 1 gram.
350°	20 hours	0·0040 gram	450°	5 hours	0·0211 gram
390	20 ,,	0·0089 ,,	467	5 ,,	0·0357 ,,
457	20 ,,	0·0693 ,,	480	5 ,,	0·0829 ,,
494	20 ,,	0·1062 ,,	514	5 ,,	0·3197 ,,
520	20 ,,	0·4185 ,,	560	5 ,,	0·4679 ,,
600	6⅔ ,,	0·5030 ,,	583	5 ,,	0·4706 ,,
			608	5 ,,	0·4846 ,,
			* 675	5 ,,	0·5108 ,,
			1070	5 ,,	0·5165 ,,

* This sample, on being again heated for 6 hours at the same temperature, lost 0·0010 gram or 0·10 per cent.

The numbers in II were obtained as the result of heating the magnesite for 5 hours, using similar samples.

On account of the small amount of calcium present in the native magnesite, this was not regarded as being suitable for the determination of the minimum temperature of complete expulsion of carbon dioxide, and for this purpose recourse was had to the artificial carbonates. The large proportions of combined water in these, on the other hand, made them less suitable for the foregoing experiments than the native carbonate.

In the case of the "light" and "crystal" carbonates, the expulsion is complete at or about 750°. The "heavy" carbonate, on the other hand, retains a little of its carbon dioxide at temperatures over 810°. The following numbers were obtained in this connection:

III

Temperature.	"Heavy." Loss from 1 gram.	"Crystal." Loss from 1 gram.	"Light." Loss from 1 gram.
700°	0·5816	—	—
750	—	0·6874	0·6013
810	0·5881	0·6880	—
867	0·5895	0·6881	0·6005
926	0·5920	0·6879	—
948	0·5927	0·6879	—
1040	0·5934	0·6897	0·6009

These artificial magnesium carbonates, as purchased for the purpose of this investigation, had the following composition:

IV

	"Heavy" carbonate (Merck), per cent.	"Crystal" carbonate (Merck), per cent.	"Light" carbonate (Merck), per cent.
Magnesia	40·81	31·18	39·91
Carbon dioxide......	21·75	20·08	21·16
Water..................	37·44	48·74	38·93

None of the three agrees in composition with the comparatively simple formulæ assigned in the text-books to the basic magnesium carbonates. The formulæ which accord best with the foregoing numbers are as follows:

"Heavy" carbonate......... $41MgO,20CO_2,83H_2O$ or otherwise
$20MgCO_3,21Mg(OH)_2,62H_2O$,

"Crystal" ,, ... $24MgO,14CO_2,85H_2O$ or
$14MgCO_3,10Mg(OH)_2,75H_2O$,

"Light" ,, ... $39MgO,19CO_2,85H_2O$ or
$19MgCO_3,20Mg(OH)_2,65H_2O$,

which would require respectively

	"Heavy," per cent.	"Crystal," per cent.	"Light," per cent.
MgO............	40·86	31·09	39·74
CO_2	21·92	19·77	21·29
H_2O	37·22	49·14	38·97

The only simple formula which could be assigned to the sample of "heavy" carbonate used would be $MgCO_3,Mg(OH)_2,3H_2O$, which would require an analytical result: $MgO = 40·82$, $CO_2 = 22·45$, $H_2O = 36·73$ per cent. These numbers, whilst sufficiently close to the experimental result in respect of magnesium, show a considerable variation from the found percentage of carbon dioxide and water.

It is still more difficult to reconcile the analytical results obtained for "light" and "crystal" carbonate with any such simple formula. For the former, the nearest would be $2MgCO_3,2Mg(OH)_2,7H_2O$, and for the latter $3MgCO_3,2Mg(OH),16H_2O$, which would correspond respectively to the following percentage compositions:

	"Light," per cent.	"Crystal," per cent.
MgO	39·23	30·67
CO_2	21·38	20·06
H_2O	39·39	49·27

Neither set of percentages, however, approaches at all closely to the experimental result. There seems, therefore, no reason for doubting that, in the case of these samples of carbonate at least, the molecular composition was much more complex than such simple formulæ would indicate.

Relative Rates of Solution of Magnesias.

The estimations described below were made, not with a view to determining the final equilibrium between magnesia and its aqueous solution, but to ascertain the relative rates at which solution took place in the case of magnesias which had previously been exposed to different temperatures. Two hundred c.c. of distilled and previously thoroughly boiled out water were placed in a thermostat at 20°, and the magnesia obtained by heating 1 gram of carbonate was placed in it. The mixture was kept at 20° for 2 hours and agitated every 5 minutes, then rapidly filtered twice through a close-textured filter, and the alkalinity of 100 c.c. of the filtrate determined by means of N/50 sulphuric acid solution, phenolphthalein being used as indicator. The end point was quite sharp except in those cases where a considerable amount of undecomposed basic carbonate still remained in the residue and partly passed into solution with the oxide.

Oxide from "Heavy" Carbonate.—The gram sample used in each experiment was kept in the electric furnace for 5 hours. The sample was introduced in each case when the temperature of the furnace was already within about 100 degrees of the final temperature desired. It was allowed to remain at or near this final temperature for at least 3 hours, repeated trials having shown that this period was more than enough to fix the character of the product, at least with respect to the rate of solution in water. In this case, the rate of solution was found to be a maximum when the substance had been heated at 835—845°, and showed a continuous diminution with each increment of temperature up to 1210°, this being the highest point at which it was found possible to maintain the furnace for a lengthened period. The diminution was most rapid between 925° and 1050°.

Oxide from "Crystal" Carbonate.—The oxide obtained by similar treatment of the "crystal" carbonate showed likewise a maximum rate of solution after being maintained at a temperature of 810—865°. As in the case of the "heavy" oxide, the rate of solution diminished when the preparation had been made at higher temperatures, but the diminution was much less rapid than in the previous case. In all the experiments made at the temperature of preparation which gave the maximum rate of solution, it was found that the "crystal" oxide invariably dissolved to a somewhat smaller extent than the "heavy" oxide. When the temperature of preparation is 950—1000°, the rates of solution are the same in the two cases; above 1000° the "crystal" oxide reacts with water faster than the other.

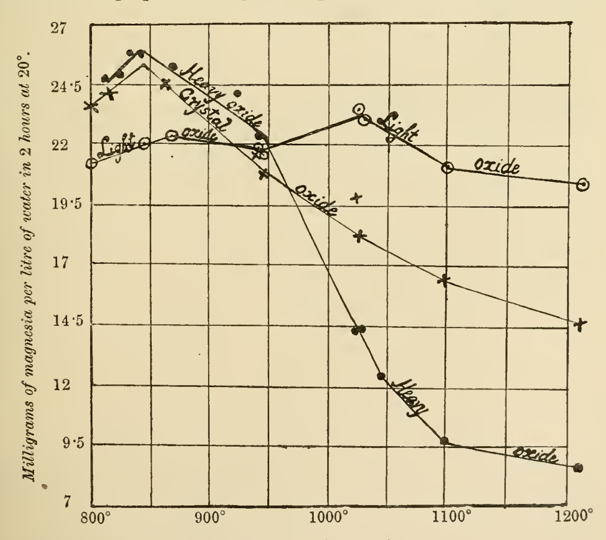
Oxide from "Light" Carbonate.—The difference between the several magnesias in respect of rate of solution is brought out still more clearly by examination of the "light oxide." In this case, the maximum rate of solution is considerably less than that of either of the preceding oxides, and it is influenced comparatively slightly by increasing the temperature of preparation. The maximum rate appears, as before, to be reached when the temperature of preparation is between 810° and 865°; but, on the other hand, repeated experiments showed a recurrence of the maximum at temperatures of preparation a little over 1000°. The rate of solution of the oxide prepared at 1057° was found to be the same as that prepared at 845°.

The experimental results for the three oxides are shown in the following tables and curves:

Rate of Solution of Magnesia.

Temperature of preparation.	Milligrams of MgO dissolved in two hours by one litre of water at 20°. "Heavy" oxide.	Milligrams of MgO dissolved in two hours by one litre of water at 20°. "Crystal" oxide.	Milligrams of MgO dissolved in two hours by one litre of water at 20°. "Light" oxide.
700°	24·48	—	—
745	—	17·28	15·24
800	—	23·52	21·36
810	24·60	24·00	23·18
822	24·80	—	—
835	25·92	—	—
845	25·92	—	22·08
865	25·20	24·48	22·32
925	24·24	—	—
940	—	21·60	21·84
945	22·56	20·76	21·60
1025	14·40	19·92	23·52
1030	14·40	18·24	23·04
1045	12·48	—	—
1057	—	—	22·08
1100	9·84	16·56	21·12
1210	8·82	14·64	20·64

Further experiment showed that the smaller numbers obtained when the oxide was prepared at higher temperatures resulted from the slow-



ness with which the product reacted with the water, and were not due to any permanent difference in solubility. Thus the heavy oxide prepared at 1025° dissolved in 2 hours to the extent of 14·40 milligrams per litre, and in 4 hours to 19·20 milligrams.

For the sake of comparison with the behaviour of the oxides obtained by direct heating of the carbonates, oxides were prepared by acting on the "heavy" and "light" carbonates with nitric acid, evaporating to dryness, and igniting the residues at 810° in the electric furnace. A sample of the "light" carbonate was heated alongside for reference. The magnesias thus obtained were carefully ground in an agate mortar, and the rates of solution determined in 2 hours at 20°. They were found to be 8·19 and 9·12 for the "nitrate" oxides as against 23·18 for that obtained by direct heating of the carbonate.

The salient features which these numbers present is the progressive change in the rate of solution of the specimens of magnesia examined as these were prepared at successively higher temperatures. The meaning to be attached to the differences of solubility in the three specimens when formed from the carbonates at the same temperature is at least open to question, since in dealing with them the error due to the very minute traces of alkaline impurity cannot be left out of account. But no such doubt arises in considering the diminution in the rate of solution of the specimens of magnesia prepared from the same carbonate at higher temperatures. Experiment shows that the loss of weight does not amount to 1 milligram per gram weight of substance in heating through a range of 300°, yet the amount which dissolves in a given time after heating shows a decrease of as much as 40—60 per cent. The only possible explanation of the result is a change in the character of the magnesia molecule itself, and the presumption is that the change is due to polymerisation. Magnesia, prepared by ignition of the carbonate at the minimum temperature, may be supposed to have a formula $(MgO)_n$, where n is a comparatively small numeral, whilst at higher temperatures its real formula would be a multiple of this. The hydration process which determines the rate of solution would then be represented by the equation:

$$(MgO)_n + n(H{\cdot}OH) = n\left(Mg{<}^{OH}_{OH}\right)$$

in the one case, and by

$$(MgO)_{mn} + mn(H{\cdot}OH) = mn\left(Mg{<}^{OH}_{OH}\right)$$

in the others. The work carried out within the scope of the present investigation does not permit of any more definite statement than this, although the differences that exist in the characters of the oxides prepared from different sources—carbonates, nitrate, and oxalate—

favour the assumption that the molecules of magnesia obtained from these under the same conditions of temperature are probably not of the same size.

Summary.—(1) The basic carbonates of magnesium are substances of high molecular weight. The samples studied in the present investigation are represented by the following formulæ:

$$20MgCO_3,21Mg(OH)_2,62H_2O,$$
$$14MgCO_3,10Mg(OH)_2,75H_2O,$$
$$19MgCO_3,20Mg(OH)_2,65H_2O,$$

or by multiples of these.

(2) These carbonates are decomposed completely into oxide when heated in an open vessel at 750° in the case of the "light" and "crystal" carbonates, but not until 810°, at least, is reached in the case of the "heavy" carbonate.

(3) The oxides prepared by heating that first obtained to different temperatures dissolve in water at different rates, the rate of solution being diminished as the temperature of preparation is increased; on the other hand, the extent of this diminution is not the same for oxides obtained from different sources. It is greatest in the case of the oxide obtained from "heavy" carbonate, less marked in the product from "crystal" carbonate, and scarcely appreciable in that from "light" carbonate.

The cost of the apparatus used in this investigation was partly defrayed by a grant from the Research Fund at the disposal of the Carnegie Trustees, to whom I desire to express my thanks.

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XXXII.—*The Latent Heat of Evaporation of Benzene and some other Compounds.*

By JAMES CAMPBELL BROWN, D.Sc.

IN a previous paper (Trans., 1903, **83**, 987), the latent heat of benzene, as determined by the method therein detailed, was not recorded because the results obtained, although concordant in different experiments and with different samples, were far from agreeing with the numbers obtained by certain other observers, Griffith and Marshall, 94·4 (*Phil. Mag.*, 1896, **41**, 1), Schiff, 93·5 (*Annalen*, 1886, **234**, 344).

The author's data nearly agreed with Jahn's determination, namely, 107·6 (*Zeit. Physikal. Chem.*, 1893, 11, 290), but this number is calculated at 0°.

Benzene labelled pure was redistilled from phosphoric oxide and the portion boiling at 80·5° taken.

		Ampere.	Volts.	
3 cells with 2 ohms resistance	giving	0·679	4·36	L=106·5
3 ,, ,, no ,,	,,	0·7754	4·92	L=106·1
3 ,, ,, 4 ohms ,,	,,	0·552	3·53	L=106·1

Another sample boiling at 80·2° was taken.

3 cells with 4 ohms resistance	giving	0·535	3·43	L=105·9
(and with a larger quantity of benzene)				L=106·0
3 cells with 3 ohms resistance	giving	0·59	3·77	L=106·7
3 ,, ,,	,,	0·58	3·74	L=106·2

A third sample boiling at 79·8° under 752 mm. pressure was taken.

3 cells with no resistance	giving	0·8525	4·885	L=106·0
4 ,, ,, ,,	,,	1·167	6·85	L=106·1
5 ,, ,, ,,	,,	1·428	8·52	L=106·0
	Average of 10 experiments..			L=106·15

It was found that in these three series of experiments the benzene used was not absolutely free from thiophen, and there may presumably have been traces of other impurities. Another sample of benzene crystals free from thiophen was specially prepared by Kahlbaum, and was again dried over phosphoric oxide immediately beforehand and redistilled; the portion taken boiled at 80·2°/759 mm., and was pure dry benzene. The flask of benzene was heated in a water-bath at 100°, the whole globe being first immersed in the water of the bath, and as soon as benzene vapour filled the jacket of the apparatus the flask was raised so that only about one-sixth of its diameter dipped in the water. There was always some difficulty in getting benzene and its homologues to boil in the tube when the current was turned on through the spiral, and it was necessary to coat the spiral of platinum wire with platinum black, and also to introduce small pieces of capillary tubing. The capillary tubing was afterwards omitted, and the spiral was wound on cross plates of mica, which served the double purpose of steadying the spiral and of assisting the discharge of vapour from the heated benzene.

Latent Heats of Pure Benzene.

	Amperes.	Volts.		Evaporating
3 cells with no resistance giving	0·885	5·18	$L = 95·08$	6·904 grams
4 ,, ,, 1 ohm ,, ,,	1·014	5·93	$L = 94·91$	9·124 ,,
4 ,, ,, no ,, ,,	1·174	6·92	$L = 94·82$	12·341 ,,
		Mean............	$L = 94·93$	(Schiff, 93·5)

$$\frac{ML}{T} = 20·92; \ \frac{ML}{\theta} = 18·1.$$

It seems probable that Griffith used pure benzene and obtained the correct number, whereas Jahn did not use the absolutely pure substance.

Toluene.

Kahlbaum's pure toluene was dried over phosphoric oxide and fractionated ; the portion boiling at 110·8° was employed. There was a similar difficulty in boiling the toluene in the spiral tube.

	Amperes.	Volts.		Evaporating
3 cells with no resistance giving	0·8748	5·223	$L = 87·56$	7·51 grams
4 ,, ,, 1 ohm ,, ,,	0·9956	6·02	$L = 87·44$	9·872 ,,
4 ,, ,, no ,, ,,	1·117	6·883	$L = 87·28$	12·683 ,,
		Mean............	$L = 87·43$	(Schiff, 83·6)

$$\frac{ML}{T} = 20·91; \ \frac{ML}{\theta} = 13·53.$$

o-*Xylene.*

Kahlbaum's purest *o*-xylene was dried over phosphoric oxide and fractionated; the greater portion boiled at 144·4°/760 mm. This sample was taken, although Beilstein gives the boiling point as 141·9°. The globe of the flask was heated in a paraffin-bath.

	Ampere.	Volts.		Evaporating
3 cells with 2 ohms resistance giving	0·605	3·28	$L = 82·42$	3·467 grams
3 ,, ,, no ,, ,,	0·792	4·31	$L = 82·5$	5·958 ,,
4 ,, ,, no ,, ,,	0·875	4·75	$L = 82·48$	7 256 ,,
		Mean............	$L = 82·47$	

$$\frac{ML}{T} = 20·91; \ \frac{ML}{\theta} = 13·83.$$

m-*Xylene.*

Kahlbaum's purest, boiling at 139·2°.

		Ampere.	Volts.		Evaporating
3 cells with 2 ohms resistance	giving	0·53	3·5	$L=81·29$	3·886 grams
3 ,, ,, no ,,	,,	0·655	4·4	$L=81·35$	5·103 ,,
4 ,, ,, no ,,	,,	0·745	5·22	$L=81·38$	6·881 ,,
		Mean...........		$L=81·34$	(Schiff, 78·3)

$$\frac{ML}{T} = 20·88; \quad \frac{ML}{\theta} = 13·92.$$

p-*Xylene.*

Kahlbaum's purest, boiling at 138·2°.

		Amperes.	Volts.		Evaporating
3 cells with 2 ohms resistance	giving	0·5975	3·78	$L=80·95$	4·019 grams
3 ,, ,, no ,,	,,	0·765	4·82	$L=80\ 98$	6·557 ,,
4 ,, ,, no ,,	,,	1·0606	6·72	$L=81·02$	12·668 ,,
		Mean...........		$L=80·98$	

$$\frac{ML}{T} = 20·84; \frac{ML}{\theta} = 13\ 89.$$

Mesitylene.

Kahlbaum's purest, boiling at 165°.

		Amperes.	Volts.		Evaporating
3 cells with 2 ohms resistance	giving	0·589	3·72	$L=74·4$	4·24 grams
3 ,, ,, no ,,	,,	0·744	4·84	$L=74·39$	6·972 ,,
4 ,, ,, no ,,	,,	1·041	6·68	$L=74·46$	13·452 ,,
		Mean...........		$L=74·42$	(Schiff, 71·7)

$$\frac{ML}{T} = 20·35; \quad \frac{ML}{\theta} = 13·92.$$

Cymene.

Kahlbaum's purest, boiling at 176·5°.

		Ampere.	Volts.		Evaporating
3 cells with 2 ohms resistance	giving	0·576	3·9	$L=67·66$	4·782 grams
3 ,, ,, no ,,	,,	0·7606	5·05	$L=67·61$	8·164 ,,
4 ,, ,, 1 ohm ,,	,,	0·919	6·24	$L=67·66$	12·207 ,,
		Mean...........		$L=67·64$	(Schiff, 66·3)

$$\frac{ML}{T} = 20·13; \quad \frac{ML}{\theta} = 13·9.$$

Cumene was not obtainable of sufficient purity to warrant an investigation of its latent heat.

The following are additions to the list of alcohols on p. 991 and of esters on p. 994 (Trans., 1903, **83**). Both were dried over anhydrous sodium sulphate and redistilled.

B. p.		Latent heat.	Mean.	*ML/T.*
101·8—102·2°	*tert.*-Amyl alcohol	{115·6°, 115·7}	115·65	27·09
155·5—156·2	Propyl *iso*valerate	{64·5, 64·53}	64·37	21·63

CHEMICAL DEPARTMENT,
THE UNIVERSITY OF LIVERPOOL.

XXXIII.—*The Constitution of Phenylmethylacridol.*

By JAMES JOHNSTON DOBBIE, D.Sc., F.R.S., and CHARLES KENNETH TINKLER.

EVIDENCE has been adduced to show that when cotarnine and hydrastinine are precipitated from an aqueous solution of their salts, the ammonium base which is probably at first formed immediately changes into a carbinol, or, in other words, the hydroxyl group is transferred from the nitrogen atom to an adjacent carbon atom,

$$\begin{array}{l}-CH:N(CH_3)X\\-CH_2\cdot CH_2\end{array} + MOH = MX + \begin{array}{l}-CH(OH)\cdot N\cdot CH_3\\-CH_2\cdot CH_2\end{array}$$

(Trans., 1903, **83**, 598; 1904, **85**, 1005).

It has long been known that on treating phenylacridine methiodide with an alkali, a substance is produced in which the iodine atom is replaced by a hydroxyl group, and it was at first supposed that this replacement takes place without any structural change, as represented by the following equation :

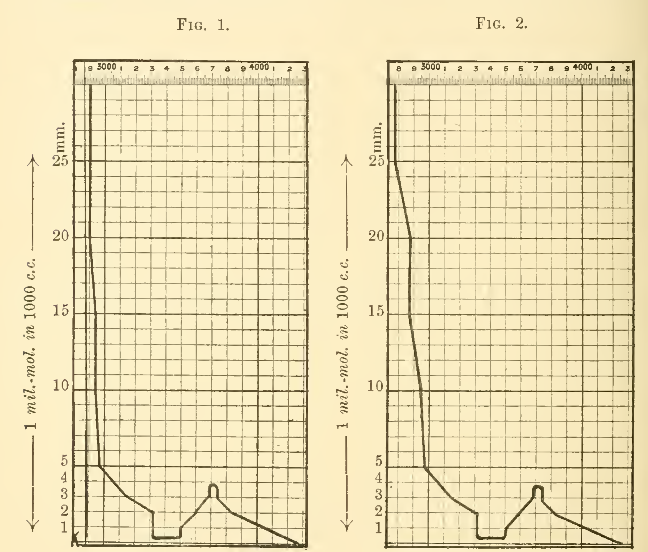
$$C_6H_4<\begin{array}{c}C(C_6H_5)\\N(CH_3)I\end{array}>C_6H_4 + MOH = MI + C_6H_4<\begin{array}{c}C(C_6H_5)\\N(CH_3)OH\end{array}>C_6H_4.$$

Hantzsch (*Ber.*, 1899, 32, 575), however, from the results of conductivity experiments, came to the conclusion that the substance produced is in reality a carbinol, a change of structure occurring at the moment of precipitation :

$$C_6H_4<\begin{array}{c}C(C_6H_5)(OH)\\N(CH_3)\end{array}>C_6H_4.$$

If this view is correct, the phenomena are closely parallel to those exhibited by cotarnine and hydrastinine. An examination of phenylacridine methiodide and of the substance obtained from it by precipitation with alkali was therefore undertaken to ascertain whether the spectra of their solutions show differences corresponding to those exhibited by the spectra of cotarnine and hydrastinine salts and their corresponding derivatives.

Phenylacridine methiodide is a dark substance which gives a yellow fluorescent solution with alcohol or water. On the addition of an



Phenylmethylacridol in ether or chloroform.

Dihydrophenylacridine.

alkali to these solutions, the colour and fluorescence entirely disappear, and in the aqueous solution a white precipitate is slowly formed. This precipitate, after recrystallisation from ether, melts at 140°. Its solution in ether or chloroform is colourless; its solution in alcohol, on the other hand, is yellow and fluorescent, the colour becoming deeper as the quantity of alcohol is increased. This substance is quite insoluble in water, but, apart from this, its analogy with cotarnine and hydrastinine obtained by precipitation from their salts is complete.

The spectra of its ethereal and chloroform solutions agree perfectly, but are quite distinct from those of the original salt, as well as from those of the alcoholic solution (Figs. 1, 3, and 4).

In the cases of cotarnine and hydrastinine, evidence in support of the carbinol formula for the solid substances was obtained from a study of the spectra of hydrocotarnine and hydrohydrastinine respectively. Similar evidence for the carbinol formula exists in the case of the substance now under discussion, which in ethereal or chloroform solu-

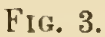
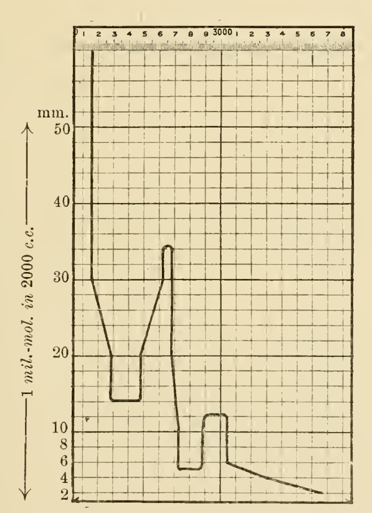


Fig. 3.



Phenylmethylacridol in 50 *per cent. methyl alcohol.*
The curve of a mixture of 75 *per cent. of dihydrophenylacridine and* 25 *per cent. of phenylacridine methiodide is practically identical with this.*

tion gives spectra that are practically identical with those of dihydrophenylacridine (Fig. 2), a colourless substance represented by the formula

$$C_6H_4 < {CH(C_6H_5) \atop NH} > C_6H_4.$$

The close resemblance between the spectra of the two substances is only explicable on the view that the structure of the substance precipitated by alkali from phenylacridine methiodide is, as represented by the carbinol formula, closely related to that of dihydrophenyl-

acridine, and that the substance is rightly named phenylmethylacridol.

In view of the results obtained with cotarnine and hydrastinine, it seemed to us probable that the alcoholic solutions of phenylmethylacridol are really mixtures of the carbinol and ammonium forms, and we found that by mixing dihydrophenylacridine and phenylacridine methiodide in various proportions, the spectra of the alcoholic solutions could be exactly reproduced. It appeared from the comparison that

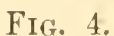
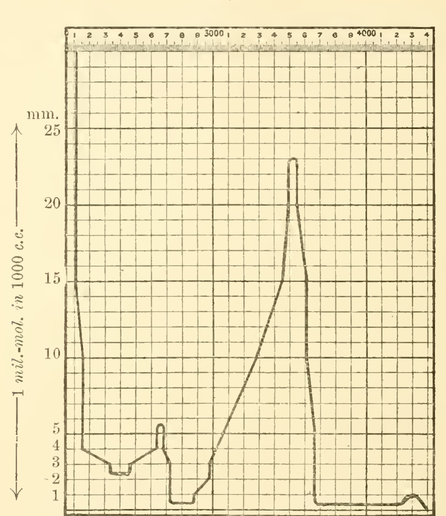


Fig. 4.



Phenylacridine methiodide.

the larger the amount of alcohol used for solution, the greater was the proportion of the ammonium base present.

A solution in methyl alcohol contains a larger proportion of the ammonium base form than an equivalent solution in ethyl alcohol. By the addition of water to the alcoholic solution, the proportion of the ammonium base form is increased. A 50 per cent. methyl-alcoholic solution (1 milligram-mol. in 2000 c.c.) was found to contain approximately 25 per cent. of ammonium form and 75 per cent. of carbinol form (Fig. 3), whilst in a 40 per cent. methyl-alcoholic solution (1 milligram-

mol. in 5000 c.c.) the whole of the substance appeared to be present in the ammonium form.

Heating also favours the production of the ammonium base form, as in the case of cotarnine and hydrastinine. The reverse change takes place on the addition of a soluble base to the alcoholic solutions; the colour and fluorescence are both discharged, and the spectra agree with those of the other colourless solutions.

Since the carbinol form is insoluble in water and cannot be changed into the ammonium form directly under the influence of water alone, it is not possible to compare the spectra of aqueous solutions of the base with those of the salts, as was done in the case of cotarnine.

THE ROYAL SCOTTISH MUSEUM,
EDINBURGH.

XXXIV.—*The Ultra-violet Absorption Spectra of certain Diazo-compounds in Relation to their Constitution.*

By JAMES JOHNSTON DOBBIE, D.Sc., F.R.S., and CHARLES KENNETH TINKLER.

WITH the discovery of the first case of isomerism in the diazo-group by Schraube and Schmidt in 1894, a controversy arose as to whether the phenomena are to be attributed to differences in structure or to differences in the arrangement of the atoms in space.

Bamberger, from a consideration of its purely chemical reactions, attributed to the potassium *iso*benzenediazotate of Schraube and Schmidt the structure of a phenylnitrosoamine, $C_6H_5{\cdot}NK{\cdot}NO$. Hantzsch, on the other hand, advanced the view that it is structurally identical with the less stable diazotate, and that the two substances are related to one another in the same way as the *syn*- and *anti*-modifications of the oximes, the unstable compound being regarded as the *syn*-, the stable as the *anti*-form :

$$\begin{matrix} C_6H_5{\cdot}N \\ \| \\ KO{\cdot}N \end{matrix} \qquad \begin{matrix} C_6H_5{\cdot}N \\ \| \\ N{\cdot}OK \end{matrix}.$$

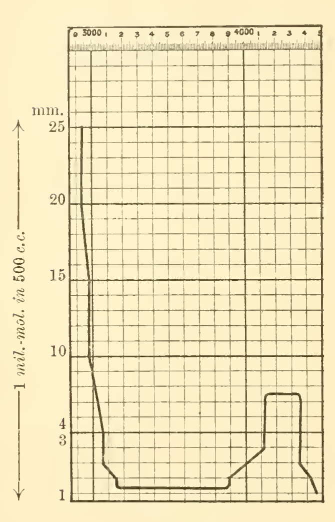
syn. *anti.*

This view received support, in Hantzsch's opinion, from the discovery of two series of diazosulphonates, the one including unstable substances, the other stable isomerides, formed from the first by re-arrangement, and closely analogous to potassium *iso*benzenediazotate. Hantzsch obtained, later, isomeric diazocyanides which he

classed as *syn-* and *anti*-modifications, the former being stable, the latter unstable substances. In all these cases, the unstable forms readily combine with β-naphthol to form dyes.

The two forms of benzaldoximes were shown by Hartley and Dobbie (Trans., 1900, 77, 509) to give identical absorption curves. Other substances similarly related have since been examined, and it has been found in all such cases that the spectra are identical, or agree more closely than those of any isomeric substances hitherto examined which differ in structure. It appeared therefore that the spectroscopic method of investigation might be applied with advantage to the diazo-compounds, since if the isomerides which have formed the subject of the above-mentioned controversy differ only in the same way as the *syn-* and *anti*-modifications of the oximes, they should give identical or nearly identical ultra-violet absorption spectra, but distinct spectra if they differ structurally.

Fig. 1.



$C_6H_5 \cdot N_2 \cdot SO_3K$.
syn- *and* anti-*Modifications.*
The absorption curve is the same for both forms.

This paper contains an account of the results which we have obtained by the examination of examples from the following groups: 1, isomeric diazosulphonates; 2, isomeric diazocyanides; 3, isomeric diazotates.

As examples of the first group, we selected the potassium salts. The less stable of these substances was obtained by Hantzsch as a reddish-yellow, crystalline precipitate by adding benzenediazonium nitrate to an alkaline solution of potassium sulphite (*Ber.*, 1894, 27, 1726). This substance dissolves easily in water to a dark yellow solution which gradually becomes lighter in colour and deposits granular crystals of the more stable isomeric salt. The solution of the less stable and more soluble salt is easily distinguished from the other, not only by its darker colour, but by the fact that it gives an intense coloration with β-naphthol. Both substances

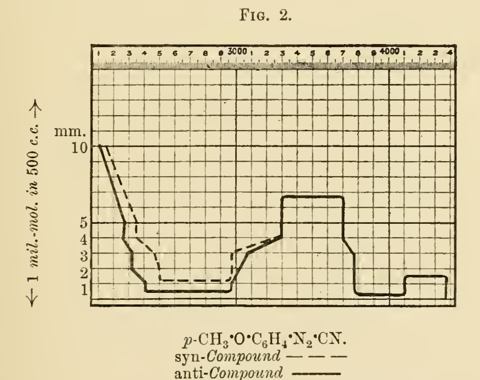
were examined immediately after solution, and were found to give spectra agreeing so closely that the absorption curves (Fig. 1) coincide, as was to be expected if the substances are related to one another in the manner indicated in the following formulæ :

$$\begin{matrix} C_6H_5\cdot N \\ \uparrow\downarrow \\ SO_3K\cdot N \end{matrix} \qquad \begin{matrix} C_6H_5\cdot N \\ \uparrow\downarrow \\ N\cdot SO_3K \end{matrix} .$$

In the second group, we examined the diazocyanides obtained respectively from *p*-anisidine and *p*-chloroaniline.

The less stable diazocyanide (m. p. 50—51°) from *p*-anisidine was obtained in accordance with the directions given by Hantzsch (*Ber.*, 1900, **33**, 2161) and converted into the stable modification (m. p.

Fig. 2.



p-$CH_3\cdot O\cdot C_6H_4\cdot N_2\cdot CN$.
syn-*Compound* — — —
anti-*Compound* ———
The two curves coincide where only one line is shown.

121—122°) by allowing it to remain until it had lost the power of reacting with β-naphthol.

The spectra of these two substances, whilst not absolutely identical, agree very closely, as will be seen by reference to their curves (Fig. 2).

Similar results were obtained with the diazocyanides derived from *p*-chloroaniline (*Ber.*, 1895, **28**, 666), the agreement between their spectra (Fig. 3) being also remarkably close, having regard to the great difficulty of obtaining the more fusible, unstable form (m. p. 29°) in a pure condition. It will be readily understood that in dealing with unstable substances such as the diazo-compounds, the perfect agreement which is obtained in the case of the more stable isomeric substances is not to be expected. The agreement, however, is so close

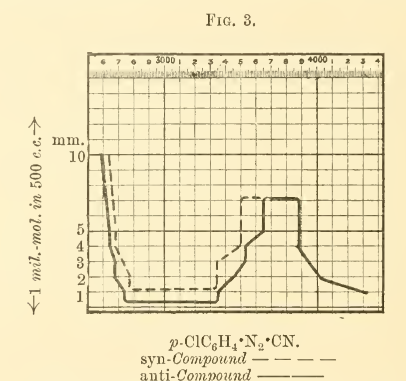
in the cases examined as to preclude the possibility of any structural difference, such as is here in question.

There is evidence of the existence of a third modification of the diazo-compounds from *p*-anisidine. By treating the *anti*-cyanide, which is a highly coloured substance, with water, Hantzsch (*loc. cit.*) obtained a practically colourless solution containing a compound which, both from the fact that it is a good electrolyte and that it is devoid of colour, he regards as a true diazonium cyanide.

$$p\text{-}CH_3{\cdot}O{\cdot}C_6H_4{\cdot}\underset{\overset{|||}{N}}{N}{\cdot}CN \; .$$

The spectra of this solution are entirely different from those of the *syn*- and *anti*-forms, and show at all events that we have in this case a substance differing structurally from these modifications.

FIG. 3.



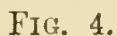
p-$ClC_6H_4{\cdot}N_2{\cdot}CN$.
syn-*Compound* — — — —
anti-*Compound* ————
The two curves coincide where only one line is shown.

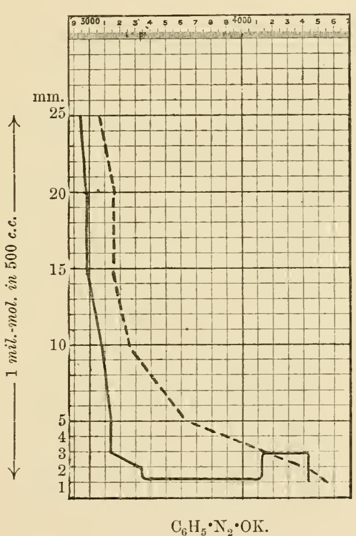
In the third group of substances, we examined, besides the two potassium compounds obtained from benzenediazonium chloride by the action of caustic potash, the potassium and sodium derivatives of diazobenzenesulphonic acid.

The less stable potassium benzenediazotate is difficult to prepare in anything approaching a pure state. We attempted the preparation by the method given by Bamberger * (*Ber.*, 1896, **29**, 461), but the product invariably contained a considerable admixture of inorganic potassium salts. We were, however, able to determine the proportion of

* According to Bamberger (*loc. cit.*), the compound prepared and analysed by Griess was really the more stable of the isomerides.

the diazo-compound present in the mixture by estimating the amount of diazonium chloride which it yielded when treated with hydrochloric acid. This was done by comparing the spectra of the solution of a weighed quantity of the mixture with those of a solution of benzene-diazonium chloride of known strength. The isomeric potassium compound of Schraube and Schmidt (*Ber.*, 1894, **27**, 514) was prepared by the method given by the discoverers. In this case, the substance is easily obtained in the pure condition. It differs from its isomeride


FIG. 4.



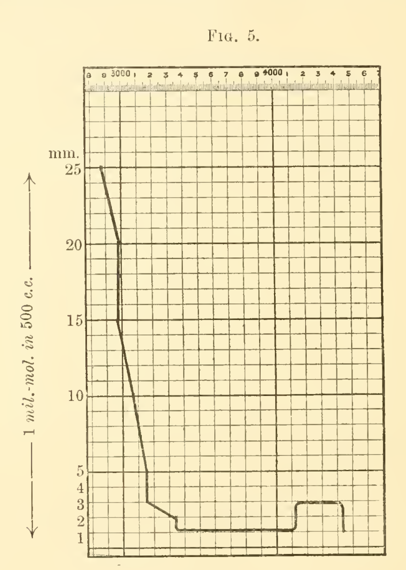
$C_6H_5 \cdot N_2 \cdot OK$.
Stable compound ———
Unstable compound — — —

in not giving a coloration with β-naphthol. Its spectra are also quite distinct, differing from those of the less stable compound in showing an absorption band and a greater amount of general absorption (Fig. 4) These two compounds therefore appear to be structural isomerides, and not *syn*- and *anti*-modifications, as Hantzsch supposes. It is possible that the less stable compound may be a *syn*-form, since it gives an azo-derivative with β-naphthol, but for the reason just stated the *iso*-compound cannot be the corresponding *anti*-modification. It might, however, possess the structure of a nitrosoamine. In this case,

its spectra would agree closely with those of phenylmethylnitrosoamine $C_6H_5{\cdot}N(CH_3){\cdot}NO$, from which it would only differ in composition in having an atom of potassium in place of the methyl group. A comparison of the spectra of the two compounds shows practically complete agreement (Figs. 4 and 5), and points to the formula $C_6H_5{\cdot}NK{\cdot}NO$ as the correct one for the more stable diazotate.

Evidence of a third modification of potassium benzenediazotate was obtained by the study of a very dilute aqueous solution of the less

Fig. 5.



Phenylmethylnitrosoamine.

stable compound. The spectra of such a solution agree closely with those of benzenediazonium chloride of the same strength, which would appear to indicate that the original compound changes under the influence of water into a true diazonium compound :

$$C_6H_5{\cdot}\underset{\displaystyle OK}{\underset{|}{N}}{:}N .$$

That some change takes place in the course of the dilution is shown by the fact that the spectrum of a layer 25 mm. thick of a solution of the less stable compound containing 1 milligram-molecule in 500 c.c.

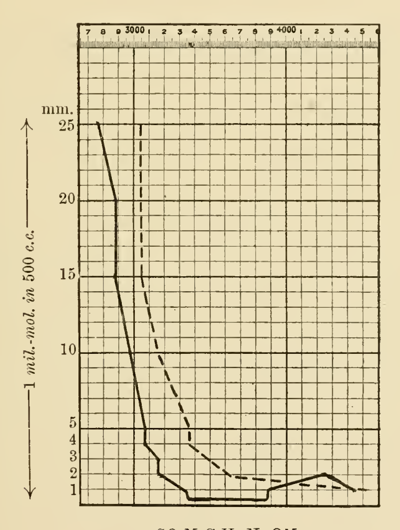
of water is different from that of a layer 5 mm. thick of a solution containing 1 milligram-molecule in 100 c.c.

It thus appears from the spectroscopic examination that there are three isomeric modifications of the compound $C_6H_5 \cdot N_2 \cdot OK$, and if the normal compound is correctly identified as a *syn*-modification, the corresponding *anti*-form remains to be discovered.

We have also examined the potassium and sodium compounds obtained from diazotised sulphanilic acid by the action of caustic alkali



FIG. 6.



$SO_3M \cdot C_6H_4 \cdot N_2 \cdot OM$.
Stable compound ————
Unstable compound — — — —

(*Ber.*, 1895, **28**, 2002). These substances differ from those just described only in possessing the group SO_3M in the nucleus, and, as was to be expected, the spectra of the isomeric substances (Fig. 6) are related in the same way as those of the preceding compounds. In this instance, the examination presents no special difficulties, as both forms can easily be obtained in the pure condition.

The purity of the salts was ascertained in this case by comparing the spectra of their solutions acidified with hydrochloric acid with those of a corresponding solution of the acid obtained by adding water

to the anhydride, $C_6H_4<{N_2 - \atop SO_3}>$. The spectra of all three solutions showed complete agreement.

The general result of our investigations has been to confirm Hantzsch's conclusions, except as regards the diazotates.

THE ROYAL SCOTTISH MUSEUM,
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XXXV.—*Action of Hydrogen Peroxide on Carbohydrates in the Presence of Ferrous Sulphate. Part V.*

By ROBERT SELBY MORRELL and ALBERT ERNEST BELLARS.

IN this communication, attempts have been made to trace the disappearance of different sugars during their oxidation by observing the diminution in the rotation angle, and from the determination of the initial and final reducing powers of the solutions, as well as their acidities, to obtain a fuller knowledge of the many oxidation stages which occur. The results of the change in the optical activity show that during successive additions of hydrogen peroxide up to 1 gram-molecule for the same weight of carbohydrate the diminution in angle is proportional to the amount of oxidising agent added. The relative decrease in the angle depends on the sugar oxidised; galactose shows a greater diminution than glucose or fructose, maltose less than sucrose, which, in turn, has a smaller decrease in angle than lactose. In the case of arabinose, it would appear as if only 50 per cent. of the sugar were acted on by 1 gram-molecule of peroxide. Rhamnose, originally dextrorotatory, becomes lævorotatory on oxidation, and the rotation is practically constant after 2 gram-atoms of oxygen have been added. This lævorotation appears to be due to the presence of a lævorotatory keto-acid. The high values of the final reducing powers must be due to the strong reducing powers of keto-acids and osoi es formed in the oxidation. The acidities of the solutions after oxidat on are not large, and are insufficient to account even for the complete formation of one monobasic hexose acid.

The smaller the yield of osazone precipitated by phenylhydrazine in the cold, the greater is the acidity of the solution. Attempts were made in the case of arabinose and rhamnose to isolate the acids formed during the oxidation. The simpler acids, formic and oxalic, were easily detected, but the more important keto-acids which were expected could not be isolated, although qualitative experiments seem to leave

little doubt of their presence. Whether these contain the same or a smaller number of carbon atoms than the parent sugar it is impossible to say.

The method of E. Fischer and E. F. Armstrong (*Ber.*, 1902, **35**, 3141) has been applied to the formation of arabinosone from arabinose, rhamnosone from rhamnose, and, by using *o*-nitrobenzaldehyde, glucosazone and rhamnosazone may be made to yield the corresponding osones.

Autoxidation experiments have been performed with benzaldehyde as inductor, whereby the oxidations of glucose and fructose to glucosone in the presence of ferrous sulphate have been slightly accelerated, but the yields of osones were very poor.

Radium emanations were found to have no influence on the oxidation of carbohydrates. The small changes in optical activity were found to be due to alteration in concentration of the sugar solutions. When the conditions were arranged so that change in the concentration of the solution became impossible, the optical activity remained constant.

Experimental.

The Change in Optical Activity of Sugar Solutions during Oxidation by Hydrogen Peroxide in the Presence of Ferrous Sulphate.

Twenty per cent. sugar solutions containing 1 per cent. of crystallised ferrous sulphate were treated with 20 volume hydrogen peroxide, and, after the addition of each one-tenth of a gram-atom of oxygen, the optical activity of the solutions was observed. It was found in the case of the hexoses that the diminution in angle was nearly proportional to the amount of hydrogen peroxide added. Glucose, fructose, and galactose were the hexoses examined, and it will be seen from the curve (Fig. 1) that the decrease in angle of the two former sugars is practically the same, whereas for galactose the diminution in the optical activity is much greater. The changes in the activity of arabinose and rhamnose solutions were observed, and it was found that the curve for arabinose lies between that of glucose and galactose, whilst a similar curve for rhamnose shows a change from a dextrorotatory to a lævorotatory power.

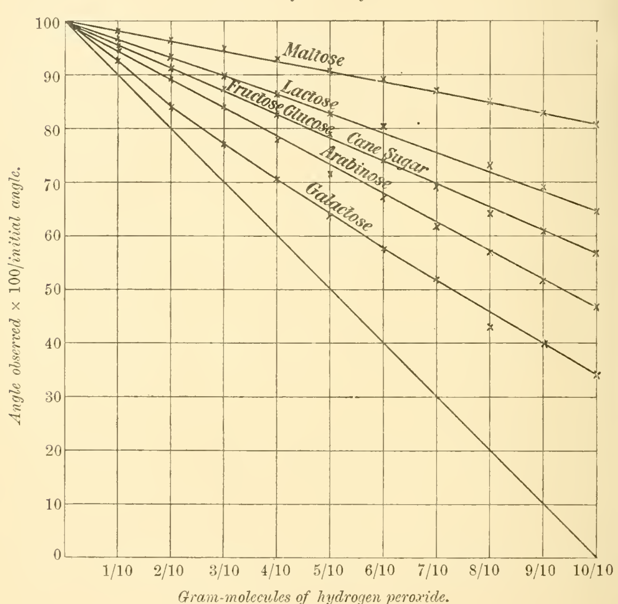
In the bioses, the diminution in optical activity is evidently connected with the hydrolytic decomposition of the sugars with acids. Maltose, lactose, and sucrose are acted on according to their power of undergoing resolution into two hexoses.

In the case of glucose and fructose, the curve showing the diminution in angle lies nearly midway between the curve expressing the decrease in angle due to dilution only and that due to the disappear-

ance of the sugar to yield inactive products. This observation cannot be taken as strictly representing a disappearance of 50 per cent. of the sugar, for, although glucosoŗe is feebly lævorotatory (E. Fischer, *Ber.*, 1889, **22**, 94), acids are formed during the oxidation, some of which may have an optical activity of the same sign as that of the parent sugar. In the case of galactose, the curve lies much closer to the dilution and loss of sugar curve than in the case of those

Fig. 1.*

Oxidation of Carbohydrates.



for glucose and fructose; moreover, the acidity at the end of the oxidation is much greater. It is unlikely that the corresponding hexose acids are formed in any quantity. Ruff (*Ber.*, 1898, **32**, 550) has shown that these acids on being heated are attacked in the presence of hydrogen peroxide and ferric salts to give aldoses containing one carbon atom less. Moreover, such aldoses in the presence of ferrous sulphate would undergo further oxidatiᴐn to give ᴄsones and acids

* Diminution in angle due to dilution has been eliminated.

containing fewer carbon atoms (Morrell and Crofts, Trans., 1899, **75**, 796). Keto-acids are more probable, since Ruff (*Ber.*, 1898, **32**, 2270) showed that in addition to *d*-arabinose, formic, glycollic, and a small quantity of a hexose acid, identified as Boutroux's oxygluconic acid, were obtained by the action of hydrogen peroxide on gluconic acid in the presence of ferric acetate.

A comparison of the curves for arabinose, namely, the calculated dilution curve, the curve representing the angular diminution during oxidation, and that due to dilution *plus* the disappearance of successive tenths of the amount of sugar up to ten-tenths, might indicate the disappearance of 50 per cent. of the sugar on the assumption that in addition to the osone only optically inactive acids are formed; glyceric acid is not produced, moreover lactic and tartaric acids have such small rotation angles compared with arabinose that their influence on the optical activity is negligible. It was thought that a further study of the oxidation of arabinose might furnish some clue as to the changes that occur during its oxidation, and at the same time might explain what took place in the case of other carbohydrates.

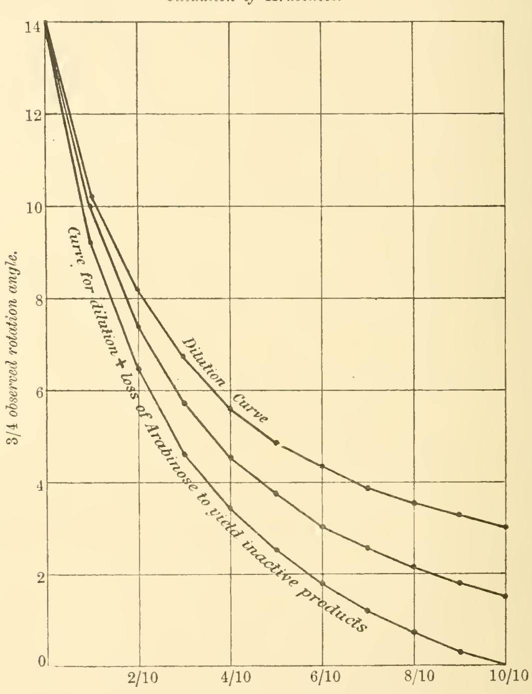
Ten grams of arabinose were dissolved in 50 c.c. of water, 0·5 gram of crystallised ferrous sulphate added, and 38·6 c.c. of hydrogen peroxide (1 c.c. = 0·0276 gram O) were introduced in one-tenths with the usual precautions. The action of the peroxide was very rapid, and in a few minutes the angle became constant, for example, at 3.15 p.m. 3·86 c.c. of hydrogen peroxide were run in, at 3.25 p.m. the angle observed was 17·08°. At 5.15 p.m. the angle was 16·89°, and 24 hours afterwards was 16·73°. The oxidation of carbohydrates is always very rapid, the hydrogen peroxide being used up as soon as it is added. Fig. 2 will show the relationship of the curve drawn from the observed data and those calculated for dilution, and for dilution *plus* disappearance of successive tenths of sugar to give inactive substances.

When the oxidation by one gram-molecule of peroxide had been completed, the acidity of the solution was determined. It was found to be 272 c.c. of *N*/10 caustic soda, or 4080 c.c. of this solution for 1 gram-molecule of arabinose; to furnish 166 grams of arabonic acid, 150 grams of arabinose would require 10 litres of *N*/10 caustic soda. It was unlikely that the oxidation had proceeded only to the formation of arabonic acid, because the reducing power of the solution had diminished from 7452 to 5767, a decrease of only one-fifth. The reducing power of the solution was estimated by means of Wood and Berry's method (*Proc. Camb. Phil. Soc.*, 1903, **12**, 98), whereby cuprous oxide is precipitated by a solution of copper potassium carbonate, and the washed cuprous oxide allowed to reduce a ferric sulphate solution; the ferrous sulphate formed was estimated by standard permanganate. The reducing power of the original sugar in the

presence of ferrous sulphate was estimated previously, the amount of ferrous sulphate being in the same proportion as that used for the oxidation of the sugar by hydrogen peroxide. The small diminution in the reducing power indicated the presence of residual sugar, of osone, and probably of a keto-acid containing 5 carbon atoms or less.

FIG. 2.

Oxidation of Arabinose.



The yield of acids forming insoluble lead salts was small because normal lead acetate precipitated only 1 gram, and basic lead acetate only 3 grams of lead salt, but it is possible that these lead salts are soluble in excess of the precipitant, as was found to be the case with lead glycollate (Morrell and Crofts, Trans., 1903, 83, 1291).

The yield of arabinosazone, after removal of the acids, was only 0·25 gram after the solution had remained for 6 hours at the ordinary temperature, but the yield was increased by 3 grams after heating the solution on the water-bath for 1 hour. Three grams of arabinosazone correspond, from experiments we have performed, with 5 grams of arabinose. The yield of arabinosone in this experiment was small, owing to the solution having remained alkaline for rather a long time during the filtration of the basic lead acetate precipitate, and E. Fischer has shown that osones are not stable in the presence of alkalis (*Ber.*, 1889, **22**, 94). In other experiments, we have found that by the oxidation of 10 grams of arabinose, 1·7 grams of arabinosazone could be obtained at the ordinary temperature after one or two hours, and 1·7 grams of arabinosazone correspond, as will be shown later, to nearly 3 grams of arabinosone. An attempt was then made to prepare a small quantity of arabinosone by using E. Fischer's method (*Ber.*, 1892, **25**, 3141), and to determine its optical activity. Ten grams of recrystallised arabinosazone were added slowly to 1800 c.c. of boiling water containing 13 grams of benzaldehyde. After $2\frac{1}{2}$ hours, the solution was filtered from unattacked arabinosazone and benzaldehyde-hydrazone, the filtrate shaken several times with ether, and concentrated to less than half its bulk in a vacuum at 50°. The liquid was again shaken several times with ether, decolorised with animal charcoal, and evaporated to a small volume. It was found to be slightly dextrorotatory, and gave an immediate precipitate at the ordinary temperature with phenylhydrazine acetate. In order to obtain a rough value of the specific rotation of the arabinosone, the syrup was evaporated to a constant weight in a platinum basin at the ordinary temperature under reduced pressure, whereby 0·2753 gram was obtained. This amount, when dissolved in 8 c.c. of water, gave a rotation of +0·245°, whence $[\alpha]_D = 7{\cdot}12°$. The contents of the polarimeter tube were warmed with the calculated quantity of phenylhydrazine acetate for $1\frac{1}{2}$ hours on the water-bath, the yield of arabinosazone precipitated was a little more than 0·1 gram. Since $[\alpha]_D$ for arabinose is 94·85°, the activity of the osone is very small compared with that of the sugar. With regard to the formation of a keto-acid from arabinose, the amounts of lead salts produced are so insignificant that further investigations would entail the use of larger quantities of the expensive carbohydrate. From 100 grams of arabinose, the yield of lead salts was so poor that their investigation was restricted to qualitative tests. The basic lead acetate precipitate was suspended in water and decomposed by hydrogen sulphide; the filtrate from lead sulphide was concentrated in a vacuum at 60° and the distillate was neutralised with calcium carbonate, a small quantity of a crystalline calcium salt obtained, which reduced mercuric chloride to mercury, but

neither reduced a Fehling's solution, nor reacted with phenylhydrazine acetate. With ferric chloride, it gave the reaction for an acetate, and on heating with dilute sulphuric acid the odours of acetic and formic acids were noticed. The residue in the distilling flask was boiled with calcium carbonate until neutral, filtered, evaporated to a small bulk, poured into alcohol, and filtered. The precipitated calcium salt reduced Fehling's solution readily, and reacted after slightly warming with phenylhydrazine to give a dark red precipitate. With *p* bromophenylhydrazine, an uncrystallisable oil was obtained. Lime water added to a solution of the calcium salt gave a white precipitate, and normal lead acetate a white precipitate, but the calcium salt did not react with aniline oxalate to give the test for glyoxylic acid.

It is advisable to give tables showing the acidities, yields of osazones, and changes in reducing power of a series of sugars, before considering the attempts to identify the acids formed from rhamnose.

One gram-mol. of sugar + one gram-mol. of peroxide.	Yield of crude osazone.	Acidity expressed in c.c. of *N*/10 NaOH.	Reducing power in c.c. of permanganate.		Diminution in reducing power. Per cent.
			Before.	After.	
Glucose	54 grams	3600	8600	6408	25·5
Fructose	63 ,,	3240	9854	8971	9
Galactose	45 ,, (hydrazo-hydrazide)	5778	7861	6152	22
Maltose	very small	4275	8550	7251	15
Lactose	practically nóne	5164	8550	8225	4
Sucrose	51 grams	3830	—	8766	—
Arabinose	25·5 ,,	4080	7452	5767	23
Rhamnose	32 ,,	4493	7500	5125	32

The yields of osazones given include that due to the osone and to the keto-acid which may have escaped precipitation by basic lead acetate. In the case of arabinose and rhamnose, the yields of osazones are larger if substituted hydrazines, such as phenylmethylhydrazine and *p*-bromophenylhydrazine are employed. The foregoing table shows that the greater the acidity in a series, the greater the diminution in angle of rotation. The reducing powers are not generally diminished more than 25 per cent., varying from 9 per cent. in the case of fructose to 32 per cent. in the case of rhamnose. It will be noticed that the reducing power of a cane sugar solution is almost that of a fructose solution, which is in agreement with the view that hydrolysis ensues before oxidation. The slight diminution in the reducing power indicated the formation of substances containing aldehyde and ketone groupings. Maltose and lactose, yielding small quantities of osones, have high acidities, due to the further oxidation of the osones, and high reducing powers owing to the presence of relatively large quantities of unattacked sugar. It is to be noticed that galactose furnishes the highest acidity number and a

reducing power, after oxidation, relatively greater than glucose, although no osone is formed, but rather a keto-hexose acid. Mr. Crofts has informed us that the dark red substance precipitated from a cold solution of oxidised galactose by phenylhydrazine contained a substance which, after repeated crystallisation from benzene, melted at 152—155°, with decomposition, and gave on analysis the following numbers.

0·1120 gave 14 c.c. moist nitrogen at 12° and 760 mm. N = 14·9.
0·1450 ,, 0·308 CO_2 and 0·0785 H_2O. C = 58·0 ; H = 6·0.
$C_{18}H_{22}O_5N_4$ requires C = 57·7 ; H = 5·9 ; N = 14·9 per cent.

Fig. 3.

Oxidation of Rhamnose.



Gram-molecules of hydrogen peroxide.

The substance, which is of a yellow colour, was deposited from benzene in nodular aggregates.

The curve for rhamnose ($[\alpha]_D$ + 7·35°) shown in Fig. 3, after the addition of 1 gram-atom of oxygen, is that for a lævorotatory solution. The angle diminished in one experiment from + 1·47° to – 0·4° for an addition of 1 gram-atom of oxygen. If the amount of the oxidising agent is increased up to 4 atoms, the fall in angle is very slow, attaining a maximum at 3 atoms of – 0·6°, and rising to – 0·4° after 4 gram-atoms of oxygen have been added. After the addition of 2 gram-atoms of oxygen, the osone was found to be present in very small quantities, and the lævorotatory power must be due to

the presence of an acid which might be rhamnonic acid. The disappearance of the osone after the addition of 2 gram-atoms of oxygen would point to the lævorotatory power being due to an acid or acids formed from the osone. The first acid formed from the osone would be a keto-acid, which would undergo further oxidation to yield two acids, oxalic or glyoxylic acid and a monobasic dihydroxy-acid; this in turn would be oxidised further, although in what way it is impossible to predict. The formation of simpler acids, the activity of which is small, from the lævorotatory keto-acid will account for the small angular diminution consequent on the addition of more than 1 gram-atom of oxygen. Reference to the table on page 286 shows that the acidity is greater than that of an arabinose solution and the diminution in reducing power is more decided. A good deal of attention has been paid to rhamnose, since the properties of this sugar have been examined more fully, and the peculiar change in sign of the rotation angle merited some consideration. In one oxidation, where 1 gram-atom of oxygen was used, it was shown that this change of sign was due to an acid, precipitated by basic lead acetate, leaving the filtrate slightly dextrorotatory. The basic lead salt, on decomposition, yielded a lævorotatory solution, which reacted slowly with phenylhydrazine to give a dark red precipitate. The amount of lead salt formed was so small that purification was impossible, and it was thought that by employing larger quantities of the oxidising agent the weight of the basic lead acetate precipitate might be increased. Two and four atoms of oxygen were used and more workable quantities of the basic lead salts were obtained. After removal of the insoluble lead salts, the solution was found to be slightly lævorotatory, and where four gram-atoms of oxygen were used the filtrate was inactive, a fact which points to the complete disappearance of the original sugar. The normal lead acetate precipitate was found to consist chiefly of lead oxalate and sulphate. These were transformed into their calcium salts. The calcium sulphate was removed by washing with water and acetic acid, and analysed; the calcium oxalate left was reduced by sodium amalgam to glyoxylic acid, which was confirmed by the Hopkins reaction with tryptophan (*Proc. Roy. Soc.*, 1901, 68, 21). Moreover, a calcium determination and estimation by standard permanganate confirmed the presence of the calcium oxalate. From the basic lead acetate precipitate, when four atoms of oxygen were used, a calcium salt was obtained which contained Ca = 18·87 and 18·91 per cent.; it reduced Fehling's solution and reacted readily with substituted hydrazines, such as phenylhydrazine and *p*-bromophenylhydrazine, but the products did not admit of recrystallisation from solvents; moreover, the salt was not calcium glyoxylate, although it answered

all the tests for glyoxylic acid except Hopkins's reaction and the aniline test. With two atoms of oxygen, the normal lead acetate precipitate yields in addition to oxalic acid a calcium salt which is partially soluble in alcohol, and the insoluble and soluble portions contain nearly the same percentage of calcium, namely, 16·87 and 17·14. It is impossible to assign with any confidence a formula to these salts, because their purity cannot be guaranteed, but it is of some interest that both calcium salts prepared in the same way react with phenylhydrazine acetate readily, and with increasing amount of hydrogen peroxide the calcium percentage is increased. Until more characteristic reactions of ketohydroxy-acids are discovered, the complete identification of acid products of the oxidation of the sugars will continue to be exceedingly difficult.

Other Methods of Preparing Osones.

As in the preparation of arabinosone by Fischer and E. F. Armstrong's method (*loc. cit.*) fairly large quantities of rhamnosone can be prepared from rhamnosazone by the action of benzaldehyde. In one experiment, 5 grams of rhamnosazone were added slowly to 1 litre of boiling water containing 5 grams of benzaldehyde, the latter being kept in solution by the previous addition of 120 c.c. of absolute alcohol. After boiling for an hour, the benzaldehydehydrazone and unattacked rhamnosazone were filtered off, and the filtrate treated in the manner described under arabinose. From the concentrated solution, nearly 0·9 gram of rhamnosazone (m. p. 178°) was obtained by treatment with phenylhydrazine acetate. It was thought that if an aldehyde were used which yielded a hydrazone more insoluble in alcohol than benzaldehydehydrazone, the formation of an osone would proceed even in absolute alcoholic solution. *o*-Nitrobenzaldehyde was employed and it was found that 1 gram of the scarlet *o*-nitrobenzaldehydehydrazone was soluble in 50 c.c. of 80 per cent. hot alcohol, and crystallised on cooling in scarlet needles. Five grams of rhamnosazone were dissolved in 100 c.c. of 90 per cent. alcohol, 8 grams of *o*-nitrobenzaldehyde and 150 c.c. of hot water added successively, and the liquid was heated for some time on the water-bath. On cooling, the osazone and unattacked *o*-nitrobenzaldehyde separated out; it seemed as if very little action had taken place between the two substances. At 125°, the two substances reacted; 5 grams of rhamnosazone dissolved in 100 c.c. of 50 per cent. alcohol and heated with 8 grams of *o*-nitrobenzaldehyde in a sealed tube for 2 hours, gave a quantity of osone which yielded 0·3 gram of rhamnosazone (m. p. 178°). If the temperature were raised to 140° and the heating prolonged to 8 hours, no osone could be detected.

When 4·5 grams of glucosazone were heated with 11·5 grams of *o*-nitrobenzaldehyde in a 55 per cent. alcoholic solution at 100° in a sealed tube, no *o*-nitrobenzaldehydehydrazone was formed; at 125° the reaction commenced, and the scarlet hydrazone appeared. The contents of the tube were diluted with water, and the unattacked glucosazone and *o*-nitrobenzaldehyde were filtered off. The last traces of *o*-nitrobenzaldehyde were removed by ether, and the aqueous solution, after concentration in a vacuum, reacted with phenylhydrazine at the ordinary temperature to give glucosazone (m. p. 205°). The yield of regenerated glucosazone was 17 per cent. of the original weight of glucosazone.

Autoxidation Experiments with Benzaldehyde.

Instead of using hydrogen peroxide as oxidiser, oxygen might be rendered active in the presence of an inductor, such as benzaldehyde. Engler and Wild (*Ber.*, 1897, **30**, 1669) state that the interaction of oxygen and benzaldehyde gives benzoyl peroxide and hydrogen peroxide. If the aldehyde alone be exposed to the oxygen, the product will be benzoic acid. Bödlander (*Ahrens' Sammlung*, **3**, 470) assumed that benzoyl hydrogen peroxide, $C_6H_5 \cdot CO \cdot O \cdot OH$, was formed, which acted as a powerful oxidising agent. It was thought that it would be interesting to investigate whether benzaldehyde would accelerate the oxidation of the sugars in the presence of ferrous sulphate.

A stream of oxygen or air was drawn slowly through a fructose solution containing benzaldehyde and traces of ferrous sulphate in suspension. The oxidation of the iron was very rapid; after a few hours, the ferrous iron reappeared, disappearing when more air was passed in. The benzaldehyde gradually darkened in colour and became pasty, but even after several days it was not completely oxidised. After 4 days' contact with oxygen, the benzaldehyde was carefully removed by ether, and the solution was freed from ether by warming to 40° in a vacuum. Addition of phenylhydrazine acetate gave an immediate turbidity and separation of glucosazone, which in 3½ hours at the ordinary temperature amounted to 0·4 gram from 10 grams of fructose and melted on recrystallisation at 202—203° (yield, 0·2 gram). A blank experiment with 2 grams of fructose in 20 c.c. of water, a drop of ferric chloride, and sodium acetate, tested with phenylhydrazine acetate, gave during the same time an exceedingly slight precipitate. In experiments conducted with glucose, it was found that the oxidation was very much slower than in the case of fructose, although when the stream of oxygen was cut off ferrous iron reappeared, which was immediately oxidised by bubbling in more oxygen. After 4 days, the benzaldehyde was removed by ether and

the solution tested for glucosone by means of phenylhydrazine acetate under exactly the same conditions as in the case of fructose. The yield of glucosazone from 15 grams of glucose was 0·2 gram (m. p. 204°), less than one-third of what was furnished by fructose. Galactose was found to be oxidised slightly under the same conditions. The benzaldehyde during the oxidation changed to a semi-solid, brown mass, as if some of the ferric iron had been absorbed into the mixture of benzaldehyde and benzoic acid. In the presence of manganese sulphate, no change could be observed.

It was noticed that on bubbling air for 3 hours through a solution of fructose containing ferrous sulphate and a few drops of glacial acetic acid the sugar had been slightly oxidised. The solution reacted with phenylhydrazine acetate at the ordinary temperature after a quarter of an hour, but the yield of osazone was very small indeed. Fructose is invariably more easily attacked by active oxygen than glucose.

From fructose, in the presence of manganese sulphate, we were unable to obtain a solution which reacted with phenylhydrazine acetate at the ordinary temperature within 3 hours. If manganese acetate was present and oxygen was bubbled in, a decided darkening was noticed which slowly disappeared, but the oxidation was apparently very slow. The addition of alum had no effect on the rate of oxidation. The experiments were carried out in diffused daylight only.

Experiments with Radium Bromide as Catalytic Agent.

Experiments on the action of radium salts were performed to find out whether the β- and γ rays from radium bromide would accelerate the oxidation of fructose by air in the presence of ferrous sulphate. Unfortunately, the results are up to the present negative, but, nevertheless, a somewhat curious effect was obtained in the course of the work. It was thought that the change would be exceedingly small and difficult to measure. From the curves given in the earlier part of the paper, it is evident that the diminution in angle is proportional to the amount of oxidising agent present. The experiments performed consisted in exposing a 20 per cent. aqueous solution of fructose, containing 1 per cent. of crystallised ferrous sulphate and 0·03 per cent. of mercuric chloride, in a thin glass dish or ebonite vessel with a mica bottom to the action of the β- and γ-rays from 5 milligrams and 20 milligrams of radium bromide. In order to prevent evaporation, the dish resting on the capsule containing the radium bromide was placed in the dark in a large bell-jar containing a vessel filled with water to which a trace of mercuric chloride had been added.

An exactly similar solution was placed in another bell-jar and kept

in the dark and at the same temperature to serve as a blank experiment. In a second series of experiments, the sugar solutions were kept in a bell-jar which contained 5 per cent. sodium chloride solution. In a third series, the radium capsule was placed over the sugar solution. The solutions were examined in an "inversion" tube, whereby a constant temperature was secured by the water-jacket of the observation tube. The polarimeter employed was a triple field apparatus, which could be read accurately to 0·02°. In a fourth series of experiments, a glass tube containing 5 milligrams of radium bromide was left in contact with a sugar solution, containing ferrous sulphate, in a sealed flask filled with oxygen and kept in the dark for several weeks. In all cases, a similar blank experiment was carried out under exactly the same conditions. In the first series of experiments, the solution over radium gained in weight, whilst the blank solution lost slightly; this loss must have been due to evaporation during the weighing of the dish. The results were independent of the nature of the vessel, and were the same whether glass or ebonite vessels were employed. In six days, 13·7495 grams of a 20 per cent. fructose solution gained 0·0695 grams, whilst the blank solution lost 0·015 gram (the solutions were weighed every day). The solution over radium showed a slight diminution in optical activity, and was less by 0·25° than the angle observed in the blank solution. After three weeks, the angle had diminished by 0·7° and was 0·47° less than that shown by the blank experiment. The two solutions possessed the same acidity, and showed no difference in their behaviour towards phenylhydrazine acetate; in neither case was there an immediate precipitate of glucosazone.

In the second series of experiments, it was found that the solution in a glass vessel over which 20 milligrams of radium were placed lost weight faster than the blank solution, and the angle increased slightly in consequence. After 3 weeks, the angles differed only by 0·48°.

In the fourth series of experiments, after 5 days there was absolutely no change in the angles observed in the solution in the flask containing 5 milligrams of radium bromide, and in the blank experiment, even after 3 weeks' exposure, there was no change in the angle. The results may be summarised as follows: oxygen does not alter the rotation of a fructose solution in the presence of ferrous sulphate when the solution is kept in a large flask in the dark even after 5 days (compare Fenton and Jackson, Trans., 1899, **85**, 10), and it does not alter the rotation of a similar fructose solution under the same conditions in the presence of a tube containing 5 milligrams of radium bromide even after 3 weeks. The changes in weight and small differences in angles observed must be due to alterations in the concentra-

tions of the solutions. Probably the emanations from the radium bromide, by setting up convection currents, accelerate the evaporation from the water to the sugar solution in the first series of experiments, and from the sugar to the salt in the second series. When the radium capsule in the bell-jar was insulated from the surrounding air by means of ebonite and thick glass, the differences in the weight of the two solutions were much diminished, and there was, after 10 days, no alteration of optical activity in the two cases. The salt solution used had a greater osmotic pressure than the fructose solution, and the presence of a trace of mercuric chloride precluded any intervention of ferments. These experiments were brought to an abrupt conclusion by the 20 milligrams of radium bromide in the capsule absorbing water through the cover and losing their radioactivity.

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XXXVI.—*The Reduction of* iso*Phthalic Acid.*

By WILLIAM HENRY PERKIN, jun., and SAMUEL SHROWDER PICKLES.

DURING the course of his classical researches on the reduction of benzene and its derivatives, Baeyer devoted much time and labour more especially to the investigation of the products formed during the reduction of phthalic acid and of terephthalic acid.

By devising new processes of reduction and employing systematic and most skilful methods of separation, Baeyer was able in both cases not only to solve the intricate problem of the nature of the reduction products, but also to establish clearly the constitutions of the many acids formed from the original reduction products by various processes of intramolecular change.

The papers in which the results of these exceedingly difficult investigations are published must always rank as among the most important in the whole range of organic chemistry.*

Whilst then the mechanism of the reduction of phthalic and tere-

* See especially *Annalen*, 1888, **245**, 103 ; 1889, **251**, 257 ; 1889, **256**, 1 ; 1890, **258**, 1, 145 ; 1891, **266**, 159 ; 1892, **269**, 145 ; 1893, **276**, 255.

phthalic acids may be said to be well understood, very little has so far been done to solve the problem in the case of *iso*phthalic acid. The first mention of the behaviour of this acid on reduction is to be found in a paper published by Baeyer in 1886 (*Ber.*, 19, 1806), in which it is stated that reduction takes place with much greater difficulty than in the case of terephthalic acid. After boiling 2 grams with sodium amalgam for 3 days, an acid was isolated which melted at 199° and gave, on analysis, numbers agreeing with those required for a tetrahydro*iso*phthalic acid. In 1891, one of the present authors (Perkin Trans., 59, 808) succeeded in preparing the *cis*- and *trans*-modifications of hexahydro*iso*phthalic acid synthetically, the process employed being the following.

Ethyl hexamethylenetetracarboxylate was first obtained by digesting the disodium derivative of ethyl pentanetetracarboxylate with methylene iodide,

$$CH_2\begin{cases}CH_2\cdot CNa(CO_2Et)_2\\CH_2\cdot CNa(CO_2Et)_2\end{cases} + CH_2I_2 = CH_2\begin{cases}CH_2\cdot C(CO_2Et)_2\\ \qquad >CH_2\\CH_2\cdot C(CO_2Et)_2\end{cases} + 2NaI,$$

and subsequently this same ester was prepared more conveniently by Perkin and Prentice (Trans., 1891, 59, 990) by acting on the disodium derivative of ethyl propanetetracarboxylate with trimethylene dibromide:

$$CH_2\begin{cases}CH_2Br\\CH_2Br\end{cases} + \begin{matrix}NaC(CO_2Et)_2\\ >CH_2\\NaC(CO_2Et)_2\end{matrix} = CH_2\begin{cases}CH_2\cdot C(CO_2Et)_2\\ \qquad >CH_2\\CH_2\cdot C(CO_2Et)_2\end{cases} + 2NaBr.$$

The hexamethylenetetracarboxylic acid obtained from this ester by hydrolysis is decomposed when heated at 200° with elimination of carbon dioxide and formation of the *cis*- and *trans*-modifications of hexahydro*iso*phthalic acid:

$$\begin{matrix}H \quad CO_2H\\ \diagdown\diagup \\ H_2\diagup\diagdown H_2\\ H_2 \quad H-CO_2H\\ \diagdown\diagup\\ H_2\end{matrix} \qquad\qquad \begin{matrix}CO_2H \quad H\\ \diagdown\diagup \\ H_2\diagup\diagdown H_2\\ H_2 \quad H-CO_2H\\ \diagdown\diagup\\ H_2\end{matrix}$$

cis (m. p. 160°). *trans* (m. p. 120°).*

Shortly after this, Baeyer and Villiger (*Annalen*, 1893, 276, 255) obtained these *cis*- and *trans*-modifications of hexahydro*iso*phthalic acid from *iso*phthalic acid by reduction, and showed that the acids thus prepared agree in their properties exactly with those which had previously been obtained synthetically.

* Further experiments on these syntheses have shown that this melting point is probably a good deal too low.

During the course of a long series of experiments on the constitution of a number of substances belonging to the camphor group, it seemed at one time probable that some of these might be derived from, or closely allied to, one of the possible tetrahydro*iso*phthalic acids.

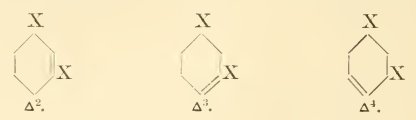
It was therefore thought advisable to prepare and characterise these, at that time, unknown acids. Preliminary experiments showed at once that the problem was an exceedingly difficult one, and all attempts which were then made to effect a separation of the mixture of acids formed by the reduction of *iso*phthalic acid with sodium amalgam were fruitless, and only served to confirm the experience of Baeyer and Villiger (*Annalen*, 1893, **276**, 259), who had previously experimented with this mixture. These authors describe the results of their experience in the following words: "Alle Versuche, aus dem rohen Reductionsproducte eine zur Untersuchung hinreichende Menge einer einheitlichen Säure zu isoliren, blieben bisher resultatlos." Since, however, the problem was an exceedingly interesting one, it was decided 4 years ago to attempt again the separation of this mixture of acids, and after many failures we were ultimately able to accomplish this. During the course of our experiments, we discovered that when the reduction is carried out under very carefully observed conditions, described in detail in the experimental part of this paper, the product consists almost entirely of two tetrahydro*iso*phthalic acids (A and B), which have approximately the same melting points and the same solubility in water and other solvents. As there was no possibility of separating these acids by crystallisation, a careful study of a long series of their salts was made, and it was then found that, although the calcium salts of both acids are soluble in water, the difference in solubility is sufficiently great to allow of their separation.

When these acids had been separated, they were readily converted into two other acids (C and D), and we can now give a short sketch of such of the properties of these acids as are of special importance in deciding their constitutions.

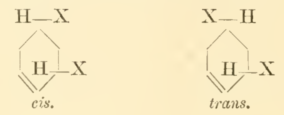
The acid (A) from the less soluble calcium salt melts at 168°, yields a solid anhydride (m. p. 78°), and, when heated with caustic potash or hydrochloric acid, is converted by intramolecular change into a very sparingly soluble tetrahydro*iso*phthalic acid (D), which melts at 244°. This acid (D) is converted into the anhydride of (A) by digesting with acetic anhydride and distilling the product under reduced pressure. The acid (B), the calcium salt of which is readily soluble in water, melts at about 165°, and, when heated with hydrochloric acid at 170°, yields a very sparingly soluble tetrahydro*iso*phthalic acid (C), which melts at 225—227°.

If we consider the question of the possible modifications of tetra-

hydro*iso*phthalic acid, we see that the following structurally different acids should exist: *



and it is also obvious that Δ^4-tetrahydro*iso*phthalic acid should be capable of existing in *cis*- and *trans*-modifications:



There are thus in all four tetrahydro*iso*phthalic acids, and it follows therefore that in isolating the acids A, B, C, and D we have prepared all the possible modifications of tetrahydro*iso*phthalic acid. Furthermore, the investigation of these acids has yielded results which, as it seems to us, point clearly, if perhaps not conclusively, to the constitution which is to be assigned to each of these four acids.

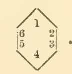
For a long time the peculiar relationships which were found to exist between these acids, relationships quite different in many ways from those met with in Baeyer's investigations of the tetrahydro-derivatives of phthalic and terephthalic acids, made the problem of assigning definite constitutional formulæ to them more than ordinarily difficult. In the first place, although it is only possible for one pair of acids to be *cis*- and *trans*-isomerides, we have found that two pairs show the reactions which are usually associated with such modifications.

(*a*) The readily soluble acid A is converted into the sparingly soluble acid D by heating with hydrochloric acid, and conversely the acid D yields the anhydride of the acid A when it is heated with acetic anhydride and the product distilled.

(*b*) The readily soluble acid B is converted into the sparingly soluble acid C when heated with hydrochloric acid.

Obviously, then, further evidence is necessary before it is possible

* $X = CO_2H$. The scheme of numbering employed in this paper is as follows:



The nomenclature and type of formula used are the same as those which Baeyer has adopted in his researches on the reduction of phthalic and terephthalic acids.

to decide which of the pairs (*a*) or (*b*) represents the *cis*- and *trans*-modifications of Δ^4-tetrahydro*iso*phthalic acid.

The considerations which have weighed most with us in our attempt to decide the constitution of these acids were the following.

The formula of the Δ^4-acid,

X

X,

contains a double linking in the $\beta\gamma$-position to one of the carboxyl groups, and it is well known from the investigations of Baeyer and others that an acid of this constitution undergoes intramolecular change when boiled with caustic potash, the double linking in this position wandering to the $\alpha\beta$-position. Now the acid D is stable to caustic potash, and therefore it cannot contain a double linking in the $\beta\gamma$-position, or, in other words, it cannot be the *trans*-modification of Δ^4-tetrahydro*iso*phthalic acid. The exclusion of the acid D leaves only one other which can possibly be this *trans*-modification, and that is the sparingly soluble acid C, which, as stated above, is obtained from the acid B by the usual process of converting a *cis*-modification into the corresponding *trans*-modification, namely, by heating with hydrochloric acid at 170°.

This argument seems to us to prove that the acids B and C must be the *cis*- and *trans*-modifications of Δ^4-tetrahydro*iso*phthalic acid.

It is next necessary to consider which of the two remaining formulæ

X	X
X	X
Δ^2.	Δ^3.

represents the acid A, and which is to be assigned to the acid D. As has already been pointed out, the double linking in D must be situated in the $\alpha\beta$-position, because the acid is stable to caustic potash. Both the above formulæ satisfy this condition, but the second seems the more probable because the Δ^2-formula still contains a double linking in the $\beta\gamma$-position to one of the carboxyl groups, whereas this is not so in the case of the Δ^3-formula. We therefore assign the Δ^2-formula to the readily soluble acid A, and the Δ^3-formula to the sparingly soluble acid D. In confirmation of this view, we may call attention to Baeyer's investigation of two acids in the phthalic series, the relationships of which are very similar to those of the Δ^2- and Δ^3-tetrahydro*iso*phthalic acids.

We refer to the case of the Δ^1- and Δ^2-tetrahydrophthalic acids:

X X Δ^1. X X. Δ^2.

The former contains the double linking between the carboxyl groups, and corresponds therefore with Δ^2-tetrahydro*iso*phthalic acid, with which it also shares the property of being very soluble in water.

When Δ^1-tetrahydrophthalic acid is digested with caustic potash it is converted, although only with difficulty, into the Δ^2-acid, the double linking wandering* from its position between the carboxyl groups (Baeyer, *Annalen*, 1890, **258**, 164). The Δ^2 tetrahydrophthalic acid thus formed has a constitution analogous to that of Δ^3-tetrahydro*iso*phthalic acid, which is produced in a similar manner from the Δ^2-acid by the action of caustic potash, and it is interesting to note that both these acids are not only characterised by being very sparingly soluble in water, but that in other respects they also show similar properties.

In this connection, the following point may be mentioned as being perhaps the most important. It has already been pointed out that Δ^3-tetrahydro*iso*phthalic acid, when digested with acetic anhydride and the product distilled, yields the anhydride of the Δ^2-acid:

X X Δ^3. gives X X. Δ^2.

that is to say, the wandering of the double linking takes place in the reverse direction to that which is brought about by treatment with caustic potash. Baeyer (*Annalen*, 1890, **258**, 202) has observed a similar change in the case of Δ^2-tetrahydrophthalic acid, since this acid, when treated with acetic anhydride and then heated, yields the anhydride of the Δ^1-acid:



These examples will suffice to illustrate the remarkable similarity in properties which exists between the Δ^1- and Δ^2-tetrahydrophthalic

* It should, however, be observed that the change of Δ^1- into Δ^2-tetrahydrophthalic acid is remarkable in this respect, that it necessitates the transference of a double linking which is in the $\alpha\beta$-position to both carboxyl groups to a position in which it is $\beta\gamma$- to one of these groups.

acids and the Δ^2- and Δ^3-tetrahydro*iso*phthalic acids, and there seems little doubt that these acids are analogously constituted.

The reasons given above and other considerations have led us to the conclusion therefore that the constitutions of the four tetrahydro*iso*phthalic acids are most probably those represented by the formulæ:

H, CO_2H	H, CO_2H	H, CO_2H	CO_2H, H
H_2, H	H_2, H_2	H_2, H_2	H_2, H_2
H_2, CO_2H	H_2, CO_2H	H, H, CO_2H	H, H, CO_2H
H_2	H	H	H
Δ^2 (m. p. 168°). Readily soluble.	Δ^3 (m. p. 244°). Sparingly soluble.	*cis*-Δ^4 (m. p. 165°). Readily soluble.	*trans*-Δ^4 (m. p. 227°). Sparingly soluble.

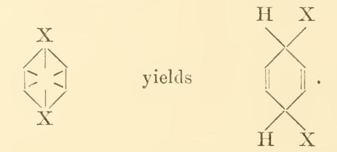
In order to obtain further confirmation of these formulæ, a long series of oxidation experiments was made, more especially with the Δ^2- and Δ^3-acids (see pp. 306, 308). It seemed possible that degradation products might result which would place the constitution of these acids beyond doubt, but this did not prove to be the case. Oxidation with permanganate has frequently been found to be of great value as a means of ascertaining the constitution of unsaturated acids, but it has repeatedly failed in the case of ring compounds. It seems to be more destructive in its action on unsaturated acids containing a closed ring, breaking them down into acids which contain a smaller number of carbon atoms than might have been expected. Baeyer (*Annalen*, 1890, **258**, 163 and 164) also found that, with one exception, oxidation with permanganate proved to be of little value as a means of obtaining evidence of the structure of the reduction products of phthalic acid.

In the experimental part of this paper will be found a description of the monobromo- and dibromo-hexahydro*iso*phthalic acids which were obtained from the various tetrahydro-acids by the addition of hydrobromic acid or of bromine, and other derivatives are also described the special mention of which is unnecessary in this introduction. We should, however, like to call attention to one interesting point, and that is to our failure to isolate even a trace of a dihydro*iso*phthalic acid from among the products of the reduction of *iso*phthalic acid with sodium amalgam. In his investigations of the reduction products of phthalic and terephthalic acids, Baeyer has shown that the products first formed are always dihydro-derivatives, and these he was able to isolate without difficulty in each case. Possibly the following considerations, based on an interesting suggestion of Baeyer (*Annalen*, 1892, **269**, 172), may supply a reason for this curious difference in the behaviour of *iso*phthalic acid.

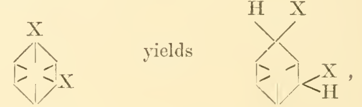
The mechanism of the process of reduction of phthalic and tere-

phthalic acids is that hydrogen atoms attach themselves in the first instance to the carbon atoms which carry the carboxyl groups, an addition which in some cases necessitates a rearrangement of the valencies. Thus the first product of the reduction of phthalic acid is $\Delta^{3 \cdot 5}$-dihydrophthalic acid :

and, in a similar manner, the first product of the reduction of terephthalic acid is $\Delta^{2 \cdot 5}$-dihydroterephthalic acid :



If this process is applied to *iso*phthalic acid, it leads to the following unsaturated scheme :



in which the valencies are unable to unite to form two double linkings, as they can do in the case of dihydrophthalic and dihydroterephthalic acids. The impossibility of forming a dihydro-derivative in this way is suggested by Baeyer as a possible explanation of the fact that *iso*phthalic acid is so much more difficult to reduce than either phthalic or terephthalic acid.

It seems to us that the impossibility of the free valencies, in the dihydro*iso*phthalic acid represented above, saturating one another may be the reason, not only why we have not been able to isolate a dihydro-acid from the products of the reduction of *iso*phthalic acid, but may also account for the fact that tetrahydro-derivatives are formed at once. If we suppose that such an intermediate substance as that represented above is first formed during the reduction with sodium amalgam, then the free valencies, which cannot saturate one another, will naturally combine with hydrogen, and thus yield at once tetrahydro*iso*phthalic acids.

Reduction of iso*Phthalic Acid.**

The method employed in this reduction was similar to that recommended by Baeyer and Villiger (*Annalen*, 1893, **276**, 258) and was briefly as follows: *iso*phthalic acid (40 grams) was dissolved in a slight excess of sodium carbonate, the solution made up to 300 c.c., and then transferred to a large porcelain beaker fitted with a mechanical stirrer. Sodium amalgam (2·5 kilograms of 3·5 per cent.) was added in small quantities at a time, the liquid being kept at 45° by means of a very small burner placed underneath the beaker and, during the whole operation, a steady and moderately rapid stream of carbon dioxide was passed. After two days, the liquid was acidified filtered from a slight flocculent precipitate,† and well shaken with three separate quantities of washed ether, by which means practically the whole of the reduced acid was easily extracted. The ethereal extract was dried over calcium chloride, evaporated to a small bulk, and the residue, which soon began to crystallise, set aside for a week or ten days, when it was found to have become almost solid.

In contact with porous porcelain, the oily mother liquor was readily absorbed, leaving a colourless, crystalline cake.

The porous plates which had accumulated from several such reductions were extracted with ether in a Soxhlet apparatus and, after distilling off the ether, the syrup was allowed to stand for some months, when it again became almost solid. After removal of the oily mother liquor by means of porous porcelain, the crystalline cake was added to that obtained in the first instance.

Lastly, the porous plates were again extracted and the extract digested with caustic potash, by which means the readily soluble mixture of acids was converted into Δ^3-tetrahydro*iso*phthalic acid (p. 307), which, being very sparingly soluble, is readily obtained pure by recrystallisation from water.

Separation of Δ^2- *and* cis-Δ^4-*Tetrahydro*iso*phthalic Acids.*

The crude solid reduction product, obtained as described in the previous section and which consisted mainly of the acids mentioned above, was dissolved in hot water and, after standing for 24 hours, filtered from some *iso*phthalic acid and small quantities of Δ^3-tetrahydro*iso*phthalic acid. The filtrate was then concentrated and left for several days until the crystalline cake which slowly formed did not

* We are indebted to Mr. T. W. D. Gregory for preparing a quantity of the reduced *iso*phthalic acid used in this research.

† This consisted mainly of unchanged *iso*phthalic acid and was used again in a subsequent reduction.

appear to increase. After filtering at the pump, the mother liquor was diluted, boiled with animal charcoal, concentrated, and again left to crystallise. By repeating this process over and over again, about 80 per cent. of the original reduction product was ultimately obtained as a hard, colourless, crystalline mass, but several months were required before the operation was complete.* The combined crops of crystals were next dissolved in much water and boiled for one hour with an excess of freshly precipitated calcium carbonate. After filtering and evaporating to a small bulk, the liquid became semi-solid owing to the separation of the sparingly soluble calcium salt of Δ^2-tetrahydro*iso*phthalic acid. This was collected at the pump, washed three times with small quantities of water, and the mother liquor again evaporated, when a further crop of the same calcium salt was obtained.

The operation was repeated many times and until no further separation of calcium salt took place; the combined crops of crystals were then treated as described in the next section.

The aqueous mother liquor of the calcium salt was acidified and repeatedly extracted with ether, and the crude *cis*-Δ^4-tetrahydro*iso*phthalic acid which remained after distilling off the ether purified as described on p. 310.

Δ^2-*Tetrahydro*iso*phthalic Acid.*

In preparing this acid, the sparingly soluble calcium salt, mentioned in the previous section, was recrystallised and then decomposed by a slight excess of hydrochloric acid. The solid acid was collected at the pump and dissolved in a little hot water, from which it separated as a glistening, crystalline powder which, under the microscope, was seen to consist of striated masses without definite shape.

0·1876 gave 0·3854 CO_2 and 0·1010 H_2O. C = 56·1; H = 6·7.
0·2090 „ 0·4332 CO_2 „ 0·1156 H_2O. C = 56·4; H = 6·1.
$C_8H_{10}O_4$ requires C = 56·4; H = 5·9 per cent.

Δ^2-*Tetrahydro*iso*phthalic acid* melts at 168° and is very readily soluble in water, alcohol, and acetic acid, but sparingly so in benzene, chloroform, light petroleum, and concentrated hydrochloric acid.

It is not very readily soluble in cold formic acid, and this solvent may, with advantage, be employed for recrystallising the acid.

A neutral solution of the ammonium salt of the acid is not

* The last mother liquor, from which no further crystals separated on standing, was digested with strong aqueous caustic potash for ten minutes. On acidifying, a considerable quantity of crude Δ^3-tetrahydro*iso*phthalic acid separated, and after decolorising with animal charcoal and twice recrystallising from water this was readily obtained pure (see p. 307).

precipitated by barium chloride, zinc sulphate, or magnesium chloride, but lead acetate causes the separation of a white, caseous precipitate which is almost insoluble in water. The *copper* salt is readily obtained by heating the aqueous solution of the acid with copper acetate and is a dark green, apparently crystalline precipitate, which is very sparingly soluble in water. When a moderately concentrated and slightly alkaline solution of the ammonium salt is mixed with calcium chloride, no precipitate is produced in the cold, but if the test-tube containing the solution is placed in boiling water the *calcium* salt gradually separates in glistening crystals. This characteristic behaviour distinguishes the Δ^2 from all the other tetrahydro*iso*phthalic acids. A quantity of the *calcium* salt was prepared and left exposed to the air for a week before being analysed. The following determinations were then made with the air-dried salt:

I. 0·3332 heated at 100° until constant lost 0·0126, or 3·8 per cent., and when heated with sulphuric acid yielded 0·1726 $CaSO_4$, or 15·3 per cent.

II. 0·3598 heated at 100° until constant lost 0·0156, or 4·3 per cent., and at 150° the total loss was 0·0634, or 17·6 per cent. On treatment with sulphuric acid, 0·1870 $CaSO_4$ resulted, or 15·3 per cent.

III. 0·4738, after drying at 100°, lost, at 160°, 0·0754, or 13·9 per cent., and yielded 0·2556 $CaSO_4$, or 15·8 per cent.

$C_8H_8O_4Ca,2\frac{1}{2}Aq.$ requires $Ca = 15·8$; $H_2O = 17·8$.

These results indicate that the air-dried calcium salt has the composition $C_8H_8O_4Ca,2\frac{1}{2}Aq.$ and that when dried at 100° two molecules of water remain and are not completely expelled until about 160°.

The *silver* salt, $C_8H_8O_4Ag_2$, was obtained, when silver nitrate was added to the warm solution of the calcium salt, as a white, very sparingly soluble precipitate, closely resembling barium sulphate in appearance. After collecting at the pump, washing well with hot water, and drying at 100°, the following results were obtained on analysis:

I. 0·3152 gave 0·1754 Ag. Ag = 55·7.
II. 0·2826 „ 0·1583 Ag. Ag = 56·0.

$C_8H_8O_4Ag_2$ requires Ag = 56·2 per cent.

The Anhydride.—Δ^2-Tetrahydro*iso*phthalic acid is very sparingly soluble in cold acetyl chloride, but on boiling in a reflux apparatus solution gradually takes place; and if, after heating for two hours, the clear solution is evaporated and the syrupy residue left over solid caustic potash in a desiccator, crystallisation soon commences.

The crystals are drained on porous porcelain and purified by recrystallisation from a mixture of benzene and light petroleum, from which the anhydride separates in well-developed, six-sided plates.

0·1914 gave 0·4450 CO_2 and 0·0929 H_2O. C = 63·4; H = 5·4.
0·1731 „ 0·4005 CO_2 „ 0·0836 H_2O. C = 63·3; H = 5·3.
$C_8H_8O_3$ requires C = 63·2; H = 5·2 per cent.

This *anhydride* melts at 78—80°, and when boiled with water is rapidly converted into the acid. It distils unchanged under 25 mm. pressure, and even under the ordinary pressure small quantities may be distilled with only very slight decomposition. It is readily soluble in warm benzene and chloroform, but rather sparingly so in cold dry ether and in methyl alcohol. The solution in chloroform is only very slowly attacked by bromine.

The *anilic acid*, $CO_2H·C_6H_8·CO·NH·C_6H_5$, is readily prepared by adding aniline to a warm solution of the anhydride in benzene, when a considerable rise of temperature takes place and crystallisation begins almost immediately. The voluminous mass of crystals is collected at the pump, washed with benzene, and recrystallised from dilute acetic acid.

0·1753 gave 8·6 c.c. of nitrogen at 13° and 767 mm. N = 5·8.
$C_{14}H_{15}O_3N$ requires N = 5·7 per cent.

This anilic acid crystallises from dilute acetic acid as a voluminous, woolly mass of flat needles, melts at about 190—192°, and is readily soluble in sodium carbonate. When heated, it loses water and is converted into a mixture of substances from which, by recrystallisation from alcohol, a substance insoluble in sodium carbonate and melting at 218° may be isolated; this was not further investigated.

2-*Bromohexahydro*iso*phthalic Acid.*—Finely divided Δ^2-tetrahydro*iso*phthalic acid dissolves readily in fuming hydrobromic acid (saturated at 0°), and, on standing, leafy crystals gradually separate; after several days, these were collected, washed with hydrobromic acid, and recrystallised from formic acid, when prismatic crystals were obtained, which melted at 187—189° and consisted of the above bromo-acid. In this behaviour, Δ^2- differs from Δ^3-tetrahydro-acid, since the latter is not attacked by hydrobromic acid in the cold. In preparing considerable quantities of the 2-bromo-acid, it was found best to heat the solution of the Δ^2-tetrahydro-acid in hydrobromic acid in a sealed tube at 100° for 5 hours, and then to pour the product into water. The precipitate was collected and recrystallised from formic acid, from which it separated in crusts, which, under the microscope, were seen to

be composed of prisms like sugar crystals, twin crystals being common.

0·1830 gave 0·1334 AgBr. Br = 31·2.

$C_8H_{11}O_4Br$ requires Br = 31·8 per cent.

*2-Bromohexahydro*iso*phthalic acid* melts at 187—189° and is readily soluble in formic acid and in warm water ; from the latter, it crystallises well in glistening prisms. When boiled with sodium carbonate, it yields a substance which melts at about 190° and is excessively soluble in water ; this substance was not further investigated.

2 : 3-*Dibromohexahydro*iso*phthalic Acid.*—When Δ^2-tetrahydro*iso*phthalic acid is exposed over dry bromine vapour for several hours, no apparent change takes place. If, however, the acid is dissolved in a considerable excess of liquid bromine and the solution, after standing for half an hour, is poured on to a sheet of glass so that the excess of bromine may rapidly evaporate, the crude 2 : 3-dibromo-acid remains as an ochre-coloured mass. This was exposed over caustic potash in a desiccator until the last traces of free bromine had been removed and then recrystallised from formic acid.

A still better method for preparing this substance is the following : the tetrahydro-acid (2 grams) is suspended in chloroform and, after cooling to 0°, mixed with a solution of bromine (2 grams) in a little chloroform. The colour of the bromine gradually disappears, and, after standing for half an hour, the solution is poured on to a flat watch-glass and the chloroform and slight excess of bromine allowed to evaporate. The residue is then recrystallised from formic acid. Specimens prepared by the above two methods gave the following results on analysis :

I. 0·2385 gave 0·2689 AgBr. Br = 47·9.
II. 0·2146 ,, 0·2431 AgBr. Br = 48·2.

$C_8H_{10}O_4Br_2$ requires Br = 48·5 per cent.

2 : 3-*Dibromohexahydro*iso*phthalic acid* melts at about 200—202° with decomposition.

Several experiments were made with the object of preparing a dihydro*iso*phthalic acid by the elimination of 2 molecules of hydrogen bromide from the 2 : 3-dibromo-acid (compare p. 310), but these were all unsuccessful. When the dibromo-acid is mixed with excess of methyl-alcoholic potash, potassium bromide separates at once, and if the solution is boiled, evaporated with water until free from methyl alcohol, and then acidified, no precipitate separates. Ether extracts a viscid oil which gradually crystallises, but from which nothing definite could be isolated.

Similar results were obtained with aqueous caustic potash and with pyridine and diethylaniline.

*Oxidation of Δ^2-Tetrahydro*iso*phthalic Acid.*—A solution of 3 grams of the pure tetrahydro-acid in 1 litre of water was rendered slightly alkaline with sodium carbonate, cooled to 0°, and oxidised with a 1 per cent. solution of permanganate, a stream of carbon dioxide being passed during the whole operation.

After removing the slight excess of permanganate with sodium sulphite, the filtrate and washings of the manganese precipitate were concentrated to 100 c.c. and then heated on the water-bath with potassium dichromate and sulphuric acid until oxidation was complete. The solution was saturated with ammonium sulphate and extracted 20 times with ether, the ethereal solution was evaporated, and the residue dissolved in a little water and heated in a sealed tube at 100° in order to decompose the malonic acid derivative which was evidently present. The contents of the tube were filtered to remove a small quantity of carbonaceous matter, evaporated to a small bulk, and tested for oxalic acid, which was found to be absent. On standing over sulphuric acid in a desiccator, the solution yielded crystals, which, after draining on porous porcelain and crystallising from ether, melted at 183° and consisted of pure *succinic acid.*

0·1031 gave 0·1537 CO_2 and 0·0489 H_2O. C = 40·7; H = 5·3.
$C_4H_6O_4$ requires C = 40·7; H = 5·1 per cent.

On mixing a small quantity of this acid with succinic acid, no alteration in the melting point was observable.

*Conversion of Δ^2-Tetrahydro*iso*phthalic Acid into Δ^3-Tetrahydro*iso*phthalic Acid.*

I. *By means of Caustic Potash.*—The pure tetrahydro-acid was dissolved in strong caustic potash solution (sp. gr. 1·25) and heated to boiling for 5 minutes. On acidifying, a very sparingly soluble acid separated, which, after recrystallisation from much water, melted at 238—242° and consisted of Δ^3-tetrahydro*iso*phthalic acid.

0·1388 gave 0·2872 CO_2 and 0·0755 H_2O. C = 56·4; H = 6·0.
$C_8H_{10}O_4$ requires C = 56·4; H = 5·9 per cent.

II. *By means of Hydrochloric Acid.*—The pure Δ^2-tetrahydro-acid (2 grams) was heated with concentrated hydrochloric acid (5 c.c.) and water (5 c.c.) in a sealed tube at 175—180° for 1 hour. No charring took place at this temperature, and the solution had deposited a crop of almost colourless crystals; it was, however, noticed in a second experiment that at 190° there is a good deal of decomposition with deposition of flocks of carbon. The crystals were collected and recrystallised from much water, and in this way a sandy precipitate was

obtained, which melted at 235—238° and consisted of Δ^3-tetrahydro*iso*-phthalic acid.

0·126 gave 0·2608 CO_2 and 0·0685 H_2O. C = 56·5 ; H = 6·0.
$C_8H_{10}O_4$ requires C = 56·4 ; H = 5·9 per cent.

Δ^3-*Tetrahydro*iso*phthalic Acid.*

This acid is produced, as was mentioned in the last section, when Δ^2-tetrahydro*iso*phthalic acid is either digested with strong aqueous caustic potash or heated with hydrochloric acid in a sealed tube at 175°. It was also obtained in considerable quantities in an experiment in which the reduction of *iso*phthalic acid with sodium amalgam was carried out at a temperature of 70°, and the alkali formed was not neutralised by passing carbon dioxide.

As a rule, it was obtained as an ochre-coloured sandy powder, which is very sparingly soluble in water and melts at about 237—240°, but by repeated recrystallisation from water and decolorising with animal charcoal the acid becomes colourless and melts at 243—244°.

Under the microscope, the crystals are seen to consist of characteristic stars with jagged edges and the appearance is quite different from that of any of the other tetrahydro*iso*phthalic acids.

0·1784 gave 0·3703 CO_2 and 0·0974 H_2O. C = 56·6 ; H = 6·1.
$C_8H_{10}O_4$ requires C = 56·4 ; H = 5·9 per cent.

Δ^3-*Tetrahydro*iso*phthalic acid* * is an exceedingly stable substance and is only slowly decomposed even when fused with caustic potash, and when heated in small quantities in a test-tube it distils apparently unchanged, since the sublimate melts without recrystallisation at 233—237°. It is sparingly soluble even in boiling water, but dissolves readily in boiling formic acid (sp. gr. 1·22) and separates on cooling in glistening, microscopic scales which have no definite shape. That it is unsaturated is shown by the fact that its solution in sodium carbonate instantaneously decolorises permanganate. The basicity of the acid

* In a short communication on the reduction products of trimesic acid (Lawrence and Perkin, Proc., 1901, **17**, 48), it was stated that tetrahydrotrimesic acid, when digested with acetic anhydride, yields a resinous double anhydride of trimesic acid and acetic acid which, on distillation, loses carbon dioxide with formation of the anhydride of tetrahydro*iso*phthalic acid :

CO_2H ; CO_2H ; CO_2H → CO, O, CO .

The substance so formed was obviously the anhydride of Δ^2-tetrahydro*iso*phthalic acid (p. 303), and the acid obtained by hydrolysing this anhydride with caustic potash and which melted at 244° was Δ^3-tetrahydro*iso*phthalic acid.

was determined by titration with decinormal caustic soda, when 0·1579 neutralised 0·0732 NaOH, whereas this amount of a dibasic acid, $C_8H_{10}O_4$, should neutralise 0·0743 NaOH. A slightly alkaline and rather dilute solution of the ammonium salt of the acid showed the following behaviour with reagents. *Silver nitrate* gave a white, caseous precipitate; *calcium chloride* gave no precipitate even on boiling; *barium chloride* also produces no precipitate in the cold, but on boiling a very sparingly soluble crystalline salt separates, which, under the microscope, is seen to consist of feathery groups of needles.

*Oxidation of Δ^3-Tetrahydro*iso*phthalic Acid.*

(*a*) *With Permanganate.*—The tetrahydro-acid (3 grams) was dissolved in a little dilute sodium carbonate and oxidised at the ordinary temperature by adding, drop by drop, a two per cent. solution of potassium permanganate. It was noticed that, when about 7 grams of permanganate had been added, the colour remained even after standing for an hour. The excess was removed by sodium sulphite, the filtrate from the manganese dioxide concentrated, acidified, and extracted repeatedly with ether. The ethereal solution deposited, on evaporation, a semi-solid mass, which was left in contact with porous porcelain until dry and then recrystallised from dilute acetic acid.

The sandy, crystalline substance thus obtained did not melt at 270°, and consisted, as the analysis shows, of iso*phthalic acid.*

0·1456 gave 0·3097 CO_2 and 0·0510 H_2O. C = 58·0 ; H = 3·9.
$C_8H_6O_4$ requires C = 57·8 ; H = 3·6 per cent.

(*b*) *With Nitric Acid.*—The tetrahydro-acid (3 grams) was heated to boiling with 20 c.c. of dilute nitric acid (sp. gr. 1·2), when vigorous oxidation set in. After one hour, the whole was allowed to stand for two days, and the crystals which had separated recrystallised from dilute acetic acid. In this way, one gram of a sparingly soluble acid was obtained which was evidently iso*phthalic acid.*

The nitric acid liquors yielded, on evaporation, oxalic acid and a gummy substance from which nothing crystalline could be obtained.

*Conversion of Δ^3- into Δ^2-Tetrahydro*iso*phthalic Acid.*

Δ^3-Tetrahydro*iso*phthalic acid is sparingly soluble in acetic anhydride in the cold, but dissolves readily on warming; the solution was boiled for two hours, the bulk of the acetic anhydride and acetic acid distilled off, and the residue left for some days in a desiccator over solid caustic potash and sulphuric acid. The syrup showed no signs of crystallising and evidently consisted of a double anhydride of

the tetrahydro-acid and acetic acid since, on treatment with water, it yielded these two acids. When this syrup was distilled under 50 mm. pressure, a pale yellow oil passed over at about 210°, leaving a large quantity of a black, resinous substance in the distilling flask. The distillate crystallised on standing and, after spreading on porous porcelain and recrystallising from light petroleum, colourless needles were obtained which melted at about 77° and consisted of the anhydride of Δ^2-tetrahydro*iso*phthalic acid (p. 303). This substance was boiled with water until completely dissolved and the solution evaporated to a small bulk, when, on cooling, pure Δ^2-tetrahydro*iso*-phthalic acid separated.

0·1448 gave 0·3006 CO_2 and 0·0777 H_2O. C = 56·6; H = 5 9.
$C_8H_{10}O_4$ requires C = 56·5; H = 5·9 per cent.

The acid thus obtained melted at 168° and yielded the sparingly soluble calcium salt so characteristic of the Δ^2-tetrahydro-acid.

4-*Bromohexahydro*iso*phthalic acid.* When Δ^3-tetrahydro*iso*phthalic acid (3 grams) is shaken with 15 c.c. of fuming hydrobromic acid, most of it dissolves and is reprecipitated unchanged on dilution with water. Addition of hydrogen bromide takes place readily, however, if the mixture of acid and hydrobromic acid is heated for one day at 100° and for a second day at 125° in the manner recommended by Baeyer (*Annalen*, 1888, **245**, 165) for the preparation of 2-bromo-hexahydroterephthalic acid from Δ^1-tetrahydroterephthalic acid.

The liquid in the tube was diluted with 5 vols. of water and allowed to stand for some hours, but only a trace of solid separated; this was removed by filtration and the solution extracted five times with ether. The ethereal solution was washed with water, dried over calcium chloride, and evaporated, when a syrup remained which showed no signs of crystallisation and, over sulphuric acid in a vacuum desiccator, frothed up owing to the escape of ether vapour. After a week, the following analysis was made :

0·2829 gave 0·2027 AgBr. Br = 30·6.
$C_8H_{11}O_4Br$ requires Br = 31·8 per cent.

When this crude 4-bromohexahydro*iso*phthalic acid is boiled with sodium carbonate and the solution acidified, a sparingly soluble acid separates which melts at 235—237° and evidently consists of Δ^3-tetrahydro*iso*phthalic acid.

3 : 4-*Dibromohexahydro*iso*phthalic Acid.* — Δ^3-Tetrahydro*iso*phthalic acid is almost insoluble in chloroform, and is only very slowly attacked when left in contact with a solution of bromine in chloroform. If, however, the finely powdered acid is exposed to dry bromine vapour for two days, it absorbs approximately the calculated quantity of

bromine, and the crude 3 : 4-dibromo-acid thus formed may be purified by recrystallisation from formic acid, from which it separates as a glistening powder, and under the microscope is seen to consist of stellate groups of well formed prisms.

0·1902 gave 0 219 AgBr. Br = 49·0.
$C_8H_{10}O_4Br_2$ requires Br = 48·5 per cent.

3 : 4-*Dibromohexahydro*iso*phthalic acid* has no definite melting point, but, when rapidly heated, decomposes at about 230° with blackening and evolution of gas.

*Dihydro*iso*phthalic Acid* (? $\Delta^{2,4}$). — The 3 : 4-dibromo-acid dissolves readily in methyl-alcoholic potash, and when the solution is boiled potassium bromide soon separates. If, after heating for half an hour, the product is diluted with water, evaporated until free from methyl alcohol, and acidified, a very insoluble precipitate, similar in appearance to barium sulphate, separates. This was collected and recrystallised from much water, from which it separated in microscopic stars. Three different specimens were analysed and it is curious that, in each case, the hydrogen determination was rather higher than that calculated for the dihydro-acid.

0·1508 gave 0·3159 CO_2 and 0·0733 H_2O. C = 57·1 ; H = 5·4.
0·1298 ,, 0·2721 CO_2 ,, 0·0627 H_2O. C = 57·2 ; H = 5·4.
0·1718 ,, 0·3590 CO_2 ,, 0·0834 H_2O. C = 57·0 ; H = 5·4.
$C_8H_8O_4$ requires C = 57·1 ; H = 4 8 per cent.

*Dihydro*iso*phthalic acid* melts at about 255° with slight previous softening, and is readily soluble in alcohol or acetone, but very sparingly so in cold water, benzene, ether, chloroform, or light petroleum. The solution of the acid in dilute sodium carbonate decolorises permanganate instantly, but the dry acid does not appear to be acted on when exposed to the vapour of dry bromine.

cis-Δ^4-*Tetrahydro*iso*phthalic Acid.*

The isolation of this acid in a state of purity proved to be a matter of great difficulty. It is contained in the mother liquors of the sparingly soluble calcium salt of the Δ^2-acid (p. 302), and, although every effort was made to remove this salt as completely as possible by crystallisation, a small amount necessarily remained dissolved. The last mother liquors of the calcium salt deposited, on acidifying, a very soluble acid, which was extracted several times with ether. After drying over anhydrous sodium sulphate, the ethereal solution, on evaporating, deposited a syrup which rapidly crystallised, and the mass became quite hard when it was left in contact with porous porcelain. By repeated recrystallisation from

water, it was ultimately found possible to isolate about 10 grams of an acid which melted at about 165°,* and when dissolved in dilute ammonia and heated with calcium chloride did not give a trace of the insoluble calcium salt of the Δ^2-acid (p. 303).

0·2092 gave 0·4332 CO_2 and 0·1156 H_2O. C = 56·4; H = 6·1.
$C_8H_{10}O_4$ requires C = 56·4; H = 5·9 per cent.

cis-Δ^4-*Tetrahydro*iso*phthalic acid* is very readily soluble in warm water, and separates on cooling in ill-shaped masses, consisting apparently of microscopic bunches of needles; it crystallises from formic acid in glistening masses, again without definite shape.

Conversion of cis-Δ^4- *into* Δ^3-*Tetrahydro*iso*phthalic Acid.*—Two grams of the *cis*-Δ^4-tetrahydro-acid were dissolved in a little dilute caustic potash, the solution was then mixed with 10 c.c. of caustic potash of sp. gr. 1·25 and heated to boiling for 10 minutes.

After evaporating nearly to dryness, the residue was dissolved in water and acidified, when a very sparingly soluble substance separated, which, after recrystallisation from much water, melted at 235—239° and consisted of nearly pure Δ^3-tetrahydro*iso*phthalic acid.

Conversion of cis-Δ^4- *into* Δ^2-*Tetrahydro*iso*phthalic acid.*—This remarkable change was brought about in the following way: The *cis*-Δ^4-acid (3 grams) was digested with 10 grams of acetic anhydride for 3 hours, transferred to a distilling flask, and the acetic acid and excess of acetic anhydride distilled off. The syrupy residue was then distilled under reduced pressure, when almost the whole passed over at about 180—210° (50 mm.) as a nearly colourless oil, a small quantity only of a dark resinous mass being left in the flask. The distillate was digested with water until dissolved and the solution concentrated, when a colourless acid gradually separated, which, after recrystallisation, melted at 166—168°.

0·1045 gave 0·2165 CO_2 and 0·0575 H_2O. C = 56·5; H = 6·1.
$C_8H_{10}O_4$ requires C = 56·4; H = 5·9 per cent.

That the acid thus obtained was Δ^2-tetrahydro*iso*phthalic acid was proved by mixing it with a specimen of the latter, when no change in the melting point could be detected. Furthermore, when a little of the acid was dissolved in dilute ammonia in a test-tube, calcium chloride added, and the test-tube placed in boiling water, the characteristic sparingly soluble calcium salt of the Δ^2-tetrahydro-acid soon began to separate.

4:5-*Dibromo*-cis-*hexahydro*iso*phthalic Acid.*—When *cis*-Δ^4-tetra-

* This melting point must only be considered as approximate, as it is obvious, for reasons stated above, that the acid may have contained traces of Δ^2-tetrahydro*iso*phthalic acid.

hydro*iso*phthalic acid is exposed over the vapour of dry bromine, it is readily converted into the dibromo-additive product, and if, after standing overnight, the excess of bromine is removed by exposure over solid caustic potash, the residue crystallises from formic acid in colourless crusts which melt at 220°.

0·2652 gave 0·3009 AgBr. Br = 48·1.
$C_8H_{10}O_4Br_2$ requires Br = 48·5 per cent.

In its behaviour towards bromine vapour, *cis*-Δ^4-tetrahydro*iso*phthalic acid differs very sharply from the Δ^2-tetrahydro-acid, since the latter is scarcely acted on under the conditions employed above (see p. 305).

trans-Δ^4-*Tetrahydro*iso*phthalic Acid.*

This acid is obtained when *cis*-Δ^4-tetrahydro*iso*phthalic acid dissolved in a little water is heated with strong hydrochloric acid in a sealed tube at 175° for 3 hours. If the temperature mentioned is not materially exceeded, the tube will contain an almost colourless, crystalline crust, but, at rather higher temperatures, decomposition sets in with separation of black, carbonaceous flocks.

The crystals were collected and recrystallised from much water, in which the acid is very sparingly soluble. The sandy powder which separated, when examined under the microscope, was seen to consist of spherical nodules.

0·1148 gave 0·2373 CO_2 and 0·0634 H_2O. C = 56·5 ; H = 6·1.
$C_8H_{10}O_4$ requires C = 56·4 ; H = 5·9 per cent.

trans-Δ^4-*Tetrahydro*iso*phthalic acid* melts at 225—227° and solidifies again at 220°, and this behaviour is not altered by repeated recrystallisation from water or formic acid. The solution of the acid in sodium carbonate reduces permanganate instantly, and when the acid is boiled with strong caustic potash it appears to be converted into Δ^3-tetrahydro*iso*phthalic acid, but this requires further confirmation.

Some of the acid was heated with fuming hydrobromic acid for 6 hours at 100°, and the clear solution, which did not give any precipitate on diluting with water, extracted with ether.

On distilling off the ether, a syrupy substance was obtained, which crystallised on standing; this was not further examined.

The remainder of the acid was finely powdered and exposed for 2 days to dry bromine vapour. The product, after standing for some days over solid caustic potash to remove excess of bromine, was crystallised from formic acid, when colourless crusts were obtained,

which had no proper melting point, but decomposed rapidly at 230—235°.

0·1766 gave 0·2011 AgBr. Br = 48·4.

$C_8H_{10}Br_2O_4$ requires Br = 48·5 per cent.

This substance is obviously 4 : 5-*dibromo*-trans-*hexahydro*iso*phthalic acid.*

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XXXVII.—*The Influence of Solvents on the Rotation of Optically Active Compounds. Part VIII. Ethyl Tartrate in Chloroform.*

By THOMAS STEWART PATTERSON.

IN Walden's interesting lecture, "Ueber das Drehungsvermögen optisch-activer Körper," which has just been published (*Ber.*, 1905, **38**, 345), there are given a number of new data relative to the influence of solvents on the rotation of optically active substances. These include, amongst others, a few values found for the rotation of ethyl tartrate in chloroform.

Some time ago I made a series of observations of a similar but much more extensive character with the same two substances. I had, and still have, the intention of carrying out analogous experiments with ethyl tartrate and a number of other solvents similar in character to chloroform, but as it is impossible at present to say when I shall be able to realise this intention, I think it advisable to publish the results hitherto obtained, and to discuss them in connection with the views expressed by Walden in his lecture.

The experimental data are collected at the end of the paper, and are represented by the curves in Fig. 1, which show the relationship between rotation and temperature for various concentrations.

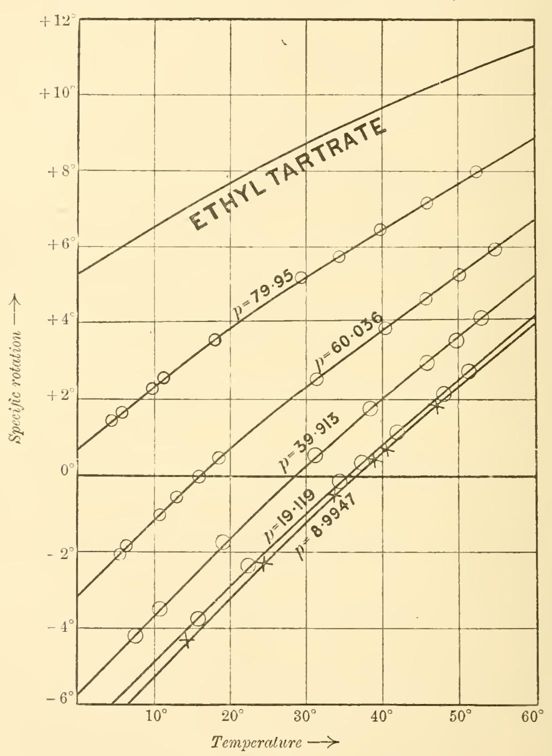
So far as the influence of temperature change is concerned, solution in chloroform has no very striking effect. The curves are all of much the same character, but it is to be noticed that in dilute solutions the rotation increases on heating somewhat more rapidly than does that of the homogeneous ester.

The influence of varying concentration, however, is very much more marked, the rotation of the ethyl tartrate being profoundly modified by admixture with chloroform. The specific rotation of the ester, which at 20° is +7·76°, is considerably depressed, in fact, it is reduced

to half value, by the addition of only 20 per cent. of the solvent. The diminution is thus at first very rapid, but as dilution proceeds the effect gradually becomes less in such a manner that beyond $p=20$ little further change in specific rotation occurs. Curves for dilutions

FIG. 1.

Rotation-temperature curves for ethyl tartrate in chloroform.

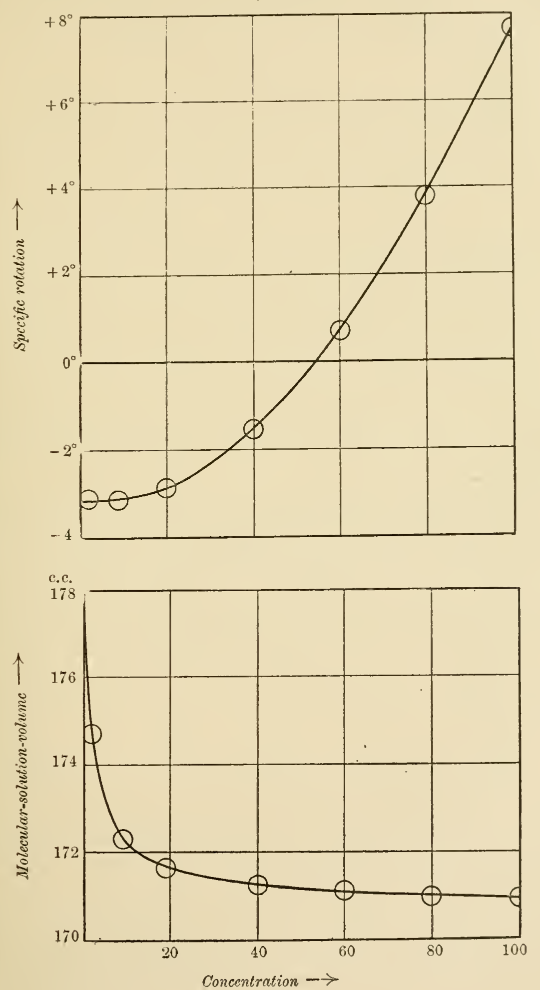


less than $p=9$ practically coincide with the lowest one shown in Fig. 1. The variation of rotation with change of concentration is shown most clearly by the upper curve of Fig. 2.

The behaviour is thus to some extent similar to that observed for mesitylene (Trans., 1902, **81**, 1099), but it is considerably more

Fig. 2.

Concentration-rotation and molecular-solution-volume curves for ethyl tartrate in chloroform.



pronounced. Both solvents appear to exert much the same maximum effect, but whereas it is only in dilute solution that mesitylene is capable of changing the sign of rotation of the dissolved ester, 97 per cent. of mesitylene being necessary at 20°, inactivity is produced in a mixture containing only 46 per cent. of chloroform at the same temperature.

From Fig. 1, it may be seen that the curve for $p = 8\cdot994$ cuts the zero axis at 36·5°. Similarly, a solution of $p = 19\cdot11$ becomes inactive at 35·5°, and those of $p = 39\cdot913$, $p = 60\cdot03$, and $p = 79\cdot95$ at 28·7°, 16·5°, and $-3°$ respectively. By plotting these values on a diagram, we find on extrapolation that an infinitely dilute solution would be inactive at 37°, so that every possible mixture of ethyl tartrate and chloroform will have a positive rotation above that temperature. By extrapolating in the opposite direction, it is found that homogeneous ethyl tartrate would become inactive between $-30°$ and $-35°$. This last result affords independent corroboration of an estimate of the temperature of inactivity of the pure ester, which was made in a previous paper (Trans., 1904, **85**, 771), the temperature formerly deduced being $-34°$.

Since Walden in his paper (*loc. cit.*, 386) gives the compositions of his solutions in concentration units (c), it is somewhat difficult to compare his results with those recorded here. There is, however, good general agreement.

Passing now to a consideration of the cause of the remarkable behaviour of chloroform solutions of ethyl tartrate, it will be seen that the present case is a very suitable one from which to judge as to the applicability of the suggestion put forward by the present author that solution-volume and rotation are closely related phenomena. It has previously been shown for a number of solvents that when the solution-volume of ethyl tartrate diminishes with dilution, a corresponding increase of rotation occurs, whilst the opposite also holds; if the solution-volume increases on dilution, the rotation diminishes.

Now, in the case of ethyl tartrate in mesitylene already referred to, the value found for the specific rotation at infinite dilution was $-3°$, the corresponding value for molecular-solution-volume being 177·4 c.c. (Trans., 1902, **81**, 1107). We should therefore expect that in chloroform, in which from Fig. 2 the specific rotation at 20° at infinite dilution is $-3\cdot2°$, the limiting value of the solution-volume should be nearly the same as for mesitylene.

Data relative to the solution-volume of ethyl tartrate in chloroform will be found on page 320. They are represented by the curve on the lower part of Fig. 2. This curve is as complete a confirmation of the suggested relationship as could be expected from the nature of the

phenomena. Dilution with chloroform gradually increases the solution-volume of the ester, the rate of increase becoming greater as the concentration of the solution diminishes, and in such a manner that on extrapolation the value at infinite dilution would lie between 177 and 178 c.c. From the shape of the curve, however, it is obviously difficult to give a very exact value.

It may be noticed that the behaviour as regards variation of rotation and of solution-volume with increasing dilution is different. The rotation at first rapidly diminishes to become almost constant at low dilutions, whilst the opposite is the case in point of solution-volume; there is only little variation in concentrated solutions and rapid variation in dilute ones.

It must be remembered, however, that it is only for the end values that we are justified in making any assumptions. At intermediate concentrations, several factors vary simultaneously, change in one masking variation in another. Such solutions are at present an unknown region, for the exploration of which rotation phenomena, when once they can be definitely interpreted, will probably prove of the greatest assistance (see Trans., 1901, **79**, 191, 192; 1902, **81**, 1100).

Walden in his paper (*loc. cit.*, p. 383) attempts to show that the variation of rotation of ethyl tartrate and some other active substances in acetone, methyl alcohol, ethyl acetate, benzene, and chloroform, bears a relationship to the degree of association of the dissolved substance determined cryoscopically or ebullioscopically. This question has already been fully discussed by the present author (Trans., 1901, **79**, 182; 1902, **81**, 1113), and little need be said about it here.

The data given by Walden are as follows, the substances being arranged in order of diminishing rotation:

Solvent.	*t*.	*p*.	$[\alpha]_D^{t}$.	M.W. (ebullioscopic).
Methyl alcohol	50°	17·94	13·82°	209·5
Acetone	50	17·32	13·36	209
Ethyl acetate	70	11·50	13·23	218·7
Benzene	70	16·92	12·06	318·5
Chloroform	50	9·91	1·08	234·8

These numbers are by no means free from objection. Temperature and concentration, which are both factors of great importance, vary considerably, whilst the concentrations of the solutions with which the molecular weights were determined were too great to allow of any result theoretically justifiable. This is especially so in the case of benzene, in which, as the present author has shown, ethyl tartrate is in very dilute solution a unimolecular substance. Walden suggests that the rotation in chloroform may be reconciled with the corre-

sponding molecular weight by supposing that there is also a constitutive influence at work, but this seems to ascribe too great a *rôle* to the latter.

The following table gives data, obtained by the present author, for ethyl tartrate in three of the above solvents, the conditions being exactly similar in each case:

Solvent.	$[\alpha]_D^{20°}$ (infinite dilution).	M.S.V.$^{20°}$ (infinite dilution).
Methyl alcohol *	+11·5°	159·3 c.c.
Benzene †	+6·1	175·1 ,,
Chloroform	−3·2	177·5 ,,

* Trans., 1901, **79**, 197. † Trans., 1902, **81**, 1107.

The agreement here is very much better, and if, as is probably the case, a constitutive factor has to be reckoned with, it is at least not sufficient to mask the relationship completely.

Experimental.

I. $p = 2·00276$.

t.	$\alpha_D^{t°}$ (400 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
5·1°	−0·730°	1·5081	−6·04°	−12·44°
5·6	−0·722	1·5070	−5·98	−12·32
16·0	−0·460	1·4878	−3·86	−7·95
19·3	−0·382	1·4815	−3·22	−6·63
35·2	−0·027	1·4517	−0·23	−0·47
41·2	+0·075	1·4405	+0·65	+1·34
45·2	+0·157	1·4330	+1·36	+2·80
52·7	+0·347	1·4190	+3·05	+6·28

II. $p = 8·9947$.

t.	$\alpha^{t°}$ (249·6 mm.).	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
14·4°	−1·42°	1·4655	−4·32°	−8·90°
16·5	−1·28	1·4617	−3·91	−8·05
24·1	−0·73	1·4480	−2·25	−4·63
33·4	−0·14	1·4320	−0·44	−0·91
38·5	+0·14	1·4230	+0·45	+0·93
40·3	+0·23	1·4199	+0·71	+1·46
46·9	+0·59	1·4081	+1·86	+3·83

III. $p = 19·119$.

t.	α (249·6 mm.)	Density.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
15·7°	−2·62°	1·4298	−3·85°	−7·93°
15·8	−2·59	1·4296	−3·79	−7·81
22·5	−1·62	1·4187	−2·39	−4·92
34·3	−0·12	1·3993	−0·18	−0·37
37·3	+0·22	1·3941	+0·33	+0·68
42·0	+0·76	1·3846	+1 15	+2·37
48·0	+1·42	1·3765	+2·16	+4·45
51·4	+1·81	1·3706	+2·77	+5·71

IV. $p = 39 \cdot 913$.

t.	$\alpha_D^{t^\circ}$ (249·6 mm.).	Density.	$[\alpha]_D^{t^\circ}$.	$[M]_D^{t^\circ}$.
7·7°	−5·75°	1·3763	−4·20°	−8·65°
10·7	−4·79	1·3720	−3·51	−7·23
19·0	−2·37	1·3603	−1·77	−3·65
31·1	+0·73	1·3434	+0·55	+1·13
38·4	+2·33	1·3330	+1·76	+3·63
45·9	+3·92	1·3223	+2·98	+6·14
49·7	+4·70	1·3172	+3·58	+7·37
52·9	+5·39	1·3123	+4·12	+8·49

V. $p = 60 \cdot 036$.

t.	$\alpha_D^{t^\circ}$ (100 mm.).	Density.	$[\alpha]_D^{t^\circ}$.	$[M]_D^{t^\circ}$.
5·6°	−1·61°	1·3203	−2·04	−4·20°
6·5	−1·47	1·3195	−1·85	−3·81
10·6	−0·81	1·3143	−1·03	−2·12
13·0	−0·45	1·3114	−0·58	−1·19
16·0	−0·01	1·3077	−0·01	−0·03
18·5	+0·35	1·3048	+0·45	+0·93
31·3	+1·97	1·2892	+2·52	+5·19
40·1	+2·96	1·2782	+3·85	+7·93
45·5	+3·53	1·2718	+4·63	+9·54
50·0	+4·00	1·2663	+5·26	+10·84
54·7	+4·48	1·2605	+5·92	+12·19

VI. $p = 79 \cdot 95$.

t.	$\alpha_D^{t^\circ}$ (100 mm.).	Density.	$[\alpha]_D^{t^\circ}$.	$[M]_D^{t^\circ}$.
4·5°	+1·47°	1·2697	+1·45°	+2·99°
5·9	1·65	1·2680	1·63	3·36
10·0	2·33	1·2635	2·30	4·74
11·3	2·60	1·2620	2·58	5·31
18·0	3·54	1·2546	3·53	7·27
29·3	5·15	1·2420	5·19	10·69
34·1	5·70	1·2370	5·77	11·89
39·8	6·33	1·2305	6·43	13·24
45·8	7·00	1·2239	7·12	14·66
52·3	7·77	1·2166	7·99	16·46

Densities Determined:

I.		II.		III.		IV.		V.		VI.	
t.	*d.*	*t.*	*d.*	*t.*	*d.*	*t.*	*d.*	*t.*	*d.*	*t.*	*d.*
12·8°	1·49369	18·0°	1·45939	17·3°	1·4272	14·5°	1·3673	13·5°	1·3114	13·7°	1·2598
26·5	1·46803	31·8	1·43531	36·3	1·3963	24·5	1·3538	26·5	1·2953	25·5	1·2466
37·0	1·4486	38·5	1·4234	51·0	1·3712	33·8	1·3401	33·2	1·2870	33·5	1·2376
51·0	1·4218	54·0	1·3956	60·0	1·3564	49·6	1·3173	57·3	1·2567	56·0	1·2270
						59·3	1·3033				

Molecular-solution-volume of Ethyl Tartrate in Chloroform (sp. gr. 1·48792 at 20°/4°).

p.	*d.*	M.S.V.$^{20°}$.	$[\alpha]_D^{20°}$.	$[M]_D^{20°}$.
0	—	177·5 c.c.	−3·20°	−6·59°
2·00276	1·48016	174·69 ,,	−3·10	−6·39
8·9947	1·45588	172·31 ,,	−3·15	−6·49
19·119	1·42274	171·62 ,,	−2·90	−5·97
39·913	1·3596	171·20 ,,	−1·55	−3·19
60·036	1·3034	171·11 ,,	+0·70	+1·44
79·95	1·2528	170·96 ,,	+3·82	+7·87
100	—	170·90 ,,	+7·76	+15·98

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XXXVIII.—*Studies in Chlorination. The Chlorination of the Isomeric Chloronitrobenzenes.*

By JULIUS BEREND COHEN and HUGH GARNER BENNETT.

IN a recent paper by Cohen and Dakin (Trans., 1904, **85**, 1274), attention was directed to the interesting relation which was found to subsist between the position assumed by the third and fourth entrant chlorine atoms obtained by chlorinating *o*- and *p*-dichlorobenzenes and the six isomeric dichlorotoluenes on the one hand, and those occupied by the two entrant nitro-groups on the other, and again by the fourth chlorine and nitro-group in the case of the 1 : 2 : 4-trichlorobenzene and the six trichlorotoluenes.

It was there proposed to extend the investigation; to study the chlorination of *m*-dichlorobenzene, which had not previously been done, as well as the chlorination of the isomeric chloronitro-compounds in order to see how far the agreement held good when nitro-groups were already present in the nucleus. The results show remarkable conformity with the above rule. We have recorded no single exception. It is true that in some cases small quantities of isomeric products were obtained, but in only one case, that of 1 : 2-dichloro-4-nitrobenzene, which offered peculiar experimental difficulties and cannot therefore be absolutely relied upon, did the principal and secondary products appear to be in the reverse order from that required by the rule.

The following table presents a summary of the results, the thick arrow indicating the principal product of chlorination where more

than one is formed. The figures within the hexagons are the melting points of the respective compounds :

The chlorination of *m*-dichlorobenzene will be dealt with elsewhere, when the whole subject of the progressive chlorination of benzene, now under investigation, has been completed. In the meantime it may be stated that the prediction in the paper already referred to (*loc. cit.*) has been completely verified, and the only products of chlorination are the 1 : 2 : 4-trichloro- and the 1 : 2 : 4 : 5-tetrachloro-benzenes.

The complete tabular summary stands as follows: the only secondary product recorded in the table is the *p*-dichloro-*p*-dinitro-benzene, the formula of which stands on the right of the last line. The remainder are the sole products of each reaction :

EXPERIMENTAL.

The method which we have used in chlorinating the nitro-compounds has been to pass a rapid stream of chlorine into the substance in presence of antimony pentachloride, which proved the most effective carrier for the purpose. Five to 10 grams of material were usually taken and, according to the rate at which chlorination proceeded, the process was conducted in the water-bath at 100° or in the oil-bath at 120—130°, the higher temperature being requisite, as the presence of a nitro-group materially retards the rate of chlorination. Above 130°, the antimony chloride rapidly volatilises and the process stops. The time required varied in different cases from 3 to 6 hours. After chlorination, the antimony chloride was removed by shaking with strong hydrochloric acid and the product was dehydrated. The subsequent treatment depended on the character of the product.

If solid, it was fractionally crystallised from alcohol; if liquid, it was fractionally distilled *in vacuo* and any solid distillate recrystallised. Any portion remaining liquid was reduced with tin and hydrochloric acid and the base or its acetyl derivative examined and, if possible, identified. Finally, the amino-compound was diazotised and the amino group replaced by chlorine. The halogen compound or compounds thus obtained were recrystallised and identified. In this way every portion of the material was submitted to a careful examination.

Chlorination of o-*Chloronitrobenzene* (m. p. 32·5°).

The chlorination was conducted at 100°, and after removing antimony chloride the product was distilled in steam. The distillate solidified and, after draining on a porous plate, melted at 27—40°. After several recrystallisations from alcohol, three fractions of constant melting point were isolated, a very minute quantity crystallising in long needles and melting at 58·5—60°, a large fraction crystallising in plates and melting at 51—54°, and a third, very soluble, and smaller fraction crystallising in needles and melting at 31—32·5°. The two larger fractions (m. p. 51—54° and 31—32·5°) were analysed with the following results:

i. (M. p. 51—54°) 0·1378 gave 0·2059 AgCl. Cl = 36·96.
ii. (M. p. 31—32·5°) 0·1670 gave 0·2543 AgCl. Cl = 37·66.
$C_6H_3O_2NCl_2$ requires Cl = 37·00 per cent.

After the above investigation had been completed, a paper by A. F. Holleman appeared (*Rec. Trav. Chim.*, 1904, **23**, 360), in which the author, on chlorinating *o*-chloronitrobenzene, obtained two substances, namely, 1 : 4-dichloro-2-nitrobenzene (m. p. 55°) and a small quantity of 1 : 2-dichloro-3-nitrobenzene (m. p. 61°). The latter is probably identical with the needles obtained by us and melting at 58·5—60°. Holleman seems, however, to have overlooked the presence of 1 : 3-dichloro-6-nitrobenzene (m. p. 33°). The principal product of the reaction is undoubtedly 1 : 4-dichloro-2-nitrobenzene, in which the entrant chlorine takes the para-position with respect to the chlorine and the meta position to the nitro-group.

Chlorination of m-*Chloronitrobenzene* (m. p. 44·5°).

Beilstein and Kurbatoff (*Annalen*, 1876, **182**, 103) found that on chlorinating nitrobenzene in presence of antimony chloride, *m*-chloronitrobenzene was first formed, and subsequently two dichloronitrobenzenes. The 1 : 4-dichloro-2-nitrobenzene was the main product, but there was also present a small quantity of uncrystallisable oil which contained a second isomeride, which they identified as the 1 : 2-dichloro-3-nitro-compound. This result has since been confirmed by Holleman (*loc. cit.*), who found that the true melting point of the second compound is 65°. The quantity of the latter was found by both observers to be very small. Holleman obtained "only a few grams" from 250 grams of nitrobenzene. We have not repeated the experiment in detail, but have merely confirmed to our satisfaction the results of the previous observers as to the main product of the reaction by separating the 1 : 4-dichloro-2-nitrobenzene (m. p. 55°).

Chlorination of p-*Chloronitrobenzene* (m. p. 83°).

The crude product, after chlorination, melted at 37—40°, and after one crystallisation from alcohol it remained stationary at 40—41°, which is the melting point of 1 : 2-dichloro-4-nitrobenzene. As the only other possible product, namely, 1 : 3-dichloro-4-nitrobenzene, melts at 33°, it is improbable that any of this compound is present.

0·1608 gave 0·2400 AgCl. Cl = 36·88.

$C_6H_3O_2NCl_2$ requires Cl = 37·00.

Chlorination of 1 : 2-*Dichloro-4-nitrobenzene* (m. p. 43°).

The substance chlorinates very slowly even at 100°. After removing antimony chloride, the product was fractionated *in vacuo*. The two fractions into which the distillate was separated were oils at the ordinary temperature, but the less volatile fraction solidified at 0°, and after draining melted at 52—54·5°. Nothing of a definite character was obtained. The process was repeated at 130°, and the resulting oil, freed by filtration from unchanged product, was directly reduced with tin and hydrochloric acid. The base thus obtained was recrystallised from 50 per cent. acetic acid, and finally from ligroin. It melted at 87—93°, and was converted into its acetyl derivative, which melts sharply at 207°. As the 3 : 4 : 5-trichloroaniline and its acetyl derivative were unknown, Mr. P. F. Crosland kindly prepared them for us from *p*-nitroaniline by the following series of processes:

NH_2		NH_2		Cl		Cl		Cl
	→	Cl, Cl	→	Cl, Cl	→	Cl, Cl	→	Cl, Cl
NO_2		NO_2		NO_2		NH_2		NHAc
		M. p. 189°.		M. p. 71°.		M. p. 94—95°.		M. p. 207—208°.

Thus the presence of 1 : 2 : 3-trichloro-5-nitrobenzene was assured. As the quantity of this substance did not appear to account for the whole of the products of chlorination, a third experiment was made as before. The substance obtained after chlorination was distilled and two fractions collected, both of which were reduced and diazotised.

After recrystallising each product separately, the first melted at 85—86° (pentachlorobenzene) and the second at 170—173° (probably impure hexachlorobenzene). The chlorination had evidently been carried too far. A fourth chlorination, which was conducted for a shorter time, gave a liquid product which was directly reduced and the amino-group replaced by chlorine. The product, which was still

liquid, was frozen and drained in the cold and then at the ordinary temperature. The small quantity which remained was recrystallised and melted sharply at 135—137·5°, which is the melting point of the 1 : 2 : 4 : 5-tetrachlorobenzene. Thus, definite proofs of the existence of two trichloronitrobenzenes were obtained, but it was impossible under circumstances in which the substances were so difficult to purify to estimate their relative quantity.

Chlorination of 1 : 4-*Dichloro*-2-*nitrobenzene* (m. p. 55°).

After chlorinating at 130°, the product was purified and reduced. Only a part of the reduced product dissolved in the hydrochloric acid, and it was separated by filtration. Each portion was diazotised separately. The insoluble fraction gave a product melting at 83—85°, and was therefore pentachlorobenzene. The soluble portion gave a chlorine derivative which melted at 137—139°, and was therefore 1 : 3 : 4 : 6-tetrachlorobenzene, which, according to Beilstein and Kurbatoff, melts at 138°; according to our own observation, at 139°. The original compound was therefore 1 : 3 : 4-trichloro-6-nitrobenzene.

Chlorination of 1 : 3-*Dichloro*-2-*nitrobenzene* (m. p. 33°).

After chlorinating at 100°, the product was distilled in steam and fractionated *in vacuo*. The first fraction solidified with difficulty, and gave no definite product. The second solidified, and after draining and crystallisation melted at 62—64°, which is the melting point of the 1 : 2 : 3 : 4-tetrachloro-5-nitrobenzene. In a second experiment, at 130°, the product was at once reduced and converted into a base which melted at 60—85°.

When the amino-group had been replaced by chlorine, the substance after crystallisation melted at 136—138°, and is therefore derived from 1 : 3 : 4-trichloro-6-nitrobenzene. No other compound was found to be present.

Chlorination of 1 : 3-*Dichloro*-5-*nitrobenzene* (m. p. 65°).

The principal object in chlorinating this compound was to determine whether the position taken by the entrant chlorine atom was situated between two chlorine atoms or between a chlorine atom and a nitro-group. It was the latter substitution which occurred.

The required material was prepared from *p*-nitroaniline, which was first converted into the dichloro-derivative, and the amino-group was then removed.

Chlorination was effected at 130°, and the product purified and distilled *in vacuo*. A part of the distillate slowly crystallised and was

separated by filtration. The solid, after recrystallisation, melted at 224—225·5°, and was therefore hexachlorobenzene (m. p. 226°).

The fact that a nitro-group can be eliminated and replaced by chlorine is mentioned by Holleman (*loc. cit.*), and a similar case is described by Schmidt and Ladner (*Ber.*, 1904, **37**, 4402), in which 9:10-bromonitrophenanthrene and *o*-bromonitrobenzene are converted into the corresponding dichloro-compounds by heating with ammonium chloride.

The liquid obtained from the product of chlorination described above was left for a few days, when a further quantity of crystals separated. These were removed by filtration and were fractionally crystallised. A further quantity of hexachlorobenzene was obtained, and also a fraction which crystallised in short, blunt needles melting at 43—44·5°. The remaining liquid was reduced and the base recrystallised, when it melted at 58—60°. The acetylated compound melted at 163—165·5°. The acetyl derivative was hydrolysed, diazotised, and the amino-group replaced by chlorine. The product, which melted at 43—45°, was sublimed and melted at 45—47·5°. There is little doubt that the compound obtained was 1 : 2 : 3 : 5-tetrachlorobenzene, which melts at 50°. This in itself is no evidence of the structure of the original trichloronitro-compound, as the same product is obtained from both of the possible isomerides.

The structure of the trichloronitro-compound is arrived at from the melting point of the base and its acetyl derivative on indirect evidence, for the 3 : 4 : 5-trichloroaniline melts at 94—95° and its acetyl derivative at 208°. The base (m. p. 58—60°) and the acetyl compound melting at 163—165·5° which we obtained do not correspond in either case with these melting points, and we therefore infer the presence of the second isomeride, of which the corresponding base is unknown.

In conclusion, we wish to thank the Research Fund Committee of the Chemical Society for a grant which has partly defrayed the cost of this research.

THE UNIVERSITY,
LEEDS.

XXXIX.—*Linin.*

By JAMES STUART HILLS, Salters' Research Fellow, and WILLIAM PALMER WYNNE.

Linum catharticum, or purging flax, is a small herb growing commonly in pastures and on banks in the British Isles. The earliest reference to its medicinal use which we have been able to discover occurs in "Gerard's Herbal," published in 1633, where Gesner, of Zurich, is quoted as identifying it, in 1555, with the helleborine of the ancients and mentioning its extensive use as a purgative by the peasantry in England.

The earliest examination of the plant seems to have been made by Pagenstecher (*Buchner's Repert. Pharm.*, 1840, **72**, 311; 1842, **76**, 313; 1843, **79**, 216), who isolated from the alcoholic extract a sparingly soluble, white substance, melting at 90—95° R., to which the name linin was given. The quantity obtained by him did not admit of an analysis being made, and the papers contain merely an account of the solubility and colour reactions of the substance with a statement that it has a bitter taste and is a purgative.

In 1845, L. A. Buchner, jun. (*ibid.*, **88**, 169), found that the alcoholic extract of the drug, freed from albuminous matters and chlorophyll, gave an increased yield of linin on the addition of hydrochloric or sulphuric acid. This result led Schröder (*Neues Repert. Pharm.*, 1861, **10**, 11) to reject the method of extraction by water or alcohol, and to isolate linin by digesting the dried herb with dilute milk of lime, acidifying the filtrate with hydrochloric acid, and extracting the resulting opalescent liquid with ether.

According to Schröder, linin when pure forms lustrous, small, white, silky crystals, melts very easily in a capillary tube, and has the characters assigned to it by Pagenstecher. The quantity at his disposal would only allow of one analysis being made, and a formula was not calculated from the results. No further reference to linin, or to the active principle of *Linum catharticum*, has been found in the literature.

As Schröder's paper is characterised by an absence of exact details, numerous variations in the method of extraction were tried in the hope of increasing the yield of linin. These will be described in detail elsewhere, and reference need only be made to the two processes which were found to give the most satisfactory results:

(i) The dried herb was percolated with 93 per cent. alcohol, and the percolate, after removal of albuminous matters and chlorophyll, boiled for an hour with hydrochloric acid. On cooling, a deposit of

crude linin was obtained, and a further small amount extracted from the filtrate by means of ether.

(ii) The dried herb was digested with one-fifth its weight of slaked lime and ten times its weight of water at 80—90° for six hours, and the filtrate, after concentration to about one-tenth its volume, boiled for five minutes with hydrochloric acid. The greater part of the linin separated in a crystalline form on cooling, and the remainder was obtained by extraction with ether.

Of the two methods, the latter was the easier to carry out and gave the better yield. Percolation with alcohol, even when prolonged for a week, did not remove the whole of the linin, as the marc, on extraction by the lime method, afforded an additional amount of the substance. The best yield obtained by the lime method on the small scale, with 500 grams of the herb, amounted to 0·135 per cent., and, on the large scale, with 21·5 kilos., to 27·1 grams of linin or 0·126 per cent.

When the boiling with hydrochloric acid was omitted, the alcoholic extract, after removal of chlorophyll and of substances precipitated by lead acetate, gave, on evaporation, a very bitter, viscid, syrupy residue without any separation of linin. Many attempts were made to obtain a crystalline separation from this residue, but without success; eventually, however, after the lapse of several months, a few hair-like needles made their appearance, but could not be identified as linin. It was free from starch, and gave only a slight reaction with Fehling's solution, but when boiled with hydrochloric or sulphuric acid afforded linin, and a solution which readily reduced Fehling's solution and contained glucose as shown by the preparation of the osazone (m. p. 205°). These results seemed to indicate the presence of a glucoside, but none could be isolated, and no evidence could be obtained to show whether the linin existed pre-formed in the syrup or was a product of hydrolysis;* it may be added that, unlike linin, the syrupy residue was a purgative.

The purification of linin was effected by crystallisation from absolute alcohol, and finally by solution in ethyl acetate followed by precipitation with light petroleum. It crystallised in long, slender, glistening needles and melted at about 205°; the melting point, however, depended very much on the rate of heating; for example, when heated slowly, linin softened at about 197°, collected on the side of the

* Our attention has been called by Dr. Jowett to a similar experience with the aqueous extract of Cascara bark. Emodin can be obtained only with difficulty from the extract by treatment with immiscible solvents, but is readily separated after the organic substances, acting as solvents, have been decomposed by the addition of an acid (Jowett, Chemical Examination of Cascara Bark, *Proc. Amer. Pharm. Assoc.*, 1904). Jowett found that emodin was dissolved by the extract of Cascara bark, and we find that linin is soluble in the "syrupy residue" to a slight extent.

capillary tube, and often did not fuse below 210—213°; when introduced into the bath at 193°, however, it melted and decomposed at 201—202°; when introduced at 202° it melted and decomposed almost sharply at 205°, and when introduced at 206° it fused at once and decomposed. On analysis, the following numbers were obtained:

0·1236 gave 0·2813 CO_2 and 0·06 H_2O. C = 62·07; H = 5·39.
0·123 „ 0·2796 CO_2 „ 0·0609 H_2O. C = 62·00; H = 5·50.
0·1253 „ 0·2856 CO_2 „ 0·0623 H_2O. C = 62·16; H = 5·52.
$C_{23}H_{24}O_9$ requires C = 62·13; H = 5·46 per cent.

The second and third of these analyses were made by independent observers. Schröder, according to the only published analysis, obtained C = 62·92; H = 4·72 per cent.

0·0716 depressed the m. p. of 11·541 benzene 0·07°. M.W. = 447.
0·0466 „ „ „ 14·455 naphthalene 0·05°. M.W. = 445.
0·8115 raised the b. p. of 11·7 c.c. acetone 0·34°. M.W. = 453.
$C_{23}H_{24}O_9$ requires M.W. = 444.

Linin dissolved fairly easily in chloroform or acetic acid, but only sparingly in methyl or ethyl alcohol, acetone, ether, or benzene in the cold, and was insoluble in light petroleum, water, or hydrochloric acid. Its alcoholic solution was only slightly bitter to the taste. It was neutral, and gave neither a coloration with ferric chloride nor a precipitate with tannic acid, lead acetate, or basic lead acetate in alcoholic solution. Boiling dilute aqueous sodium hydroxide dissolved it, forming a pale yellow solution, from which it was precipitated unchanged on the addition of hydrochloric or sulphuric acid; it may, therefore, be a lactone. With concentrated sulphuric acid, it gave a deep purple coloration, as observed by Pagenstecher, the colour fading when the solution was kept or diluted with water, and a grey flocculent precipitate being produced. The solution in chloroform did not decolorise bromine, but a bromo-derivative, which could not be obtained pure, was formed by the action of bromine on linin mixed with acetic acid.

In view of the possibility that linin was formed by the hydrolysis of a glucoside, attempts were made to acetylate it by means of acetic anhydride, alone and with sodium acetate, and of acetyl chloride, but without success. In one experiment with acetyl chloride a product was obtained which after crystallisation from alcohol melted at 220°, but after two more crystallisations at 203°. Whether in this case an acetyl derivative, easily hydrolysed by alcohol, had been formed must be left uncertain owing to the want of material. A benzoyl derivative could not be obtained by the use of the Schotten-Baumann method.

The presence of methoxyl groups in linin was established by the Zeisel method, the apparatus employed being of the form described by W. H. Perkin, sen. (Trans., 1903, **83**, 1367), supplemented by the inclusion of bulbs containing red phosphorus to prevent traces of iodine being carried over into the alcoholic silver nitrate.

0·27 gave 0·5535 AgI. OMe = 27·09.
0·3092 ,, 0·6423 AgI. OMe = 27·46.
$C_{19}H_{12}O_5(OMe)_4$ requires OMe = 27·94 per cent.

All attempts to isolate a definite substance from the demethylated residue in the distilling flask were fruitless.

On fusion of linin with 12 times its weight of potassium hydroxide at 175—180° for 15 minutes, hydrogen was evolved, and the product, after neutralisation, gave an acid distillate, which, on titration with caustic soda, was found to contain an amount of acid equivalent, when calculated as acetic acid, to 10 per cent. by weight of the substance employed. The acid could not be identified, and nothing definite could be obtained from the remainder of the product.

Pagenstecher found that linin on treatment with nitric acid became reddish-brown with evolution of gas, but he could not detect the formation of oxalic acid as a product of the oxidation. The behaviour of linin with nitric acid of various strengths, and with a mixture of nitric and sulphuric acids, was studied, and oxalic acid found to be the only recognisable product. With nitric acid (sp. gr. 1·28), a purple coloration was obtained in the cold, accompanied by a brisk evolution of gas, the linin dissolving to form a red solution.

As no intermediate product of oxidation could be obtained with nitric acid, recourse was had to potassium permanganate as an oxidising agent. This was found to effect the oxidation most readily when added to a solution of linin in 5 per cent. aqueous sodium hydroxide, but the results were disappointing, for although a crystalline substance melting at 179° and quite different in appearance from linin was obtained when the addition of permanganate was stopped after 10 atomic proportions of oxygen had been used, careful examination showed it to be impure linin. Oxalic acid proved to be the only recognisable oxidation product obtained by the use of permanganate.

Addendum.—Since this paper was communicated to the Society, Dr. Henry has called our attention to the remarkable similarity between linin and picropodophyllin, which was re-examined by Dunstan and Henry in the course of their investigation of the constituents of Indian and American *Podophyllum* (Trans., 1898, **73**, 213). The mean percentage composition of the two substances is practically the same, although the proportion of methoxyl contained in them is different.

Linin, $C_{23}H_{24}O_9$, M. W. 444. C = 62·08 ; H = 5·46 ; OMe = 27·28.
Picropodophyllin, $C_{15}H_{14}O_6$. C = 61·80 ; H = 5·38 ; OMe = 21·54.

A determination of the molecular weight of picropodophyllin is not recorded. Both substances give a bromo-derivative, yield oxalic acid as the only recognisable oxidation product, produce the same colorations with nitric and sulphuric acids, and dissolve in alcoholic sodium hydroxide, forming solutions which gelatinise on treatment with dilute acetic acid. Linin, however, melts at about 205° and picropodophyllin at 227°, whilst, as determined by Dr. Henry, to whom our thanks are due for making the comparison, a mixture of equal parts of the two melts at 184°. The recognition of similar non-purgative compounds in *Linum catharticum* and *Podophyllum*, and the failure to isolate the purgative principle of either, renders the further investigation of their proximate constituents of much interest.

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XL.—*The Influence of Temperature on the Interaction between Acetyl Thiocyanate and Certain Bases. Thiocarbamides, including Carboxy-aromatic Groups.*

By the late ROBERT ELLIOTT DORAN ; compiled by AUGUSTUS EDWARD DIXON.

Introduction [by the Compiler].

As the result of investigations which have now been carried on for several years in the chemical laboratory of Queen's College, Cork, a considerable body of evidence has been accumulated, going to establish amongst certain acyl thiocyanates the existence of a peculiar kind of tautomerism, which is characterised by the power exhibited by these substances of behaving either as such or as thiocarbimides, according to the conditions under which they are caused to interact (Trans., 1904, **85**, 807). Until comparatively recently, it had not been suspected that temperature alone might be a determining factor in these tautomeric phenomena ; for although it is well known to effect the change of unsaturated hydrocarbon thiocyanates into the isomeric

thiocarbimides, no such permanent change has yet been observed in the case of thiocyanates of distinctly acidic radicles.

The discovery that Miquel's "acetyl thiocyanate" (*Ann. Chim. Phys.*, 1877, [v], **11**, 295), when interacting with aniline, behaves at high temperatures principally as thiocarbimide, whilst at low temperatures it exchanges to a large extent the thiocarbimidic character for that of a thiocyanate, occurred fortuitously during the course of some experiments made in order to determine the capacity possessed by certain acidic groups of expelling others from combination. Acetylphenylthiocarbamide being required in connection with this work, its preparation was conducted by mixing at the ordinary temperature of the laboratory benzene solutions of acetyl thiocyanate (prepared from acetyl chloride and lead thiocyanate) and aniline. Forty per cent. only was obtained of the theoretical yield, reckoned from the weight of acetyl chloride employed, and calculated on the basis of the equations:

1. $2CH_3{\cdot}COCl + Pb(SCN)_2 = PbCl_2 + 2CH_3{\cdot}CO{\cdot}NCS.$
2. $CH_3{\cdot}CO{\cdot}NCS + C_6H_5{\cdot}NH_2 = CH_3{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5.$

A similar result followed on repeating the process, and since acetyl thiocyanate is somewhat prone to decomposition, during another experiment the reagents were surrounded by running cold water. However, the effect of this precaution was that a smaller yield was obtained than when it was not taken.

Again the experiment was tried, with constituents heated beforehand to 40°; a much better yield was now produced, which was improved still further by mixing the solutions at temperatures near their respective boiling points, the combination in these circumstances being somewhat violent.

Following up these results, an inquiry was commenced for the purpose of determining quantitatively the course of the interaction at different temperatures, and the general conclusions were summarised in a brief preliminary note (Proc., 1904, **20**, 20). The intention was to refrain from fuller publication until sufficient data should be available to permit of the graphic plotting of the results; but unhappily the progress of this research has been interrupted by Mr. Doran's untimely death.

His note-book, containing the record of a number of experiments on this subject, together with a few hitherto unpublished observations in connection with his work on the chlorocarbonates (Trans., 1896, **69**, 324; 1901, **79**, 906), has been handed to me for compilation, in order that the scientific results might be preserved, for, unfortunately, these had not been incorporated in the form of a paper. In the present communication, therefore, the experimental data are the author's; for the rest, the compiler alone is responsible. (A. E. D.)

Part I.

Acetyl Thiocyanate and Aniline.

Except in a few cases, specifically mentioned below, the general method of procedure, when working at low or moderate temperatures, was as follows: a weighed quantity of acetyl chloride, dissolved in anhydrous benzene, was heated with excess of dry lead thiocyanate until the solution ceased to give the reactions of chlorine. After separating the insoluble lead salts at the pump, the liquor was treated with aniline, dissolved in benzene, and added from a burette until two molecular proportions of base were present for each molecular proportion of acetyl chloride taken, or until the odour of acetyl thiocyanate was no longer perceptible. After a short time, the benzene mother liquor was poured off from the precipitate, and the solution allowed to evaporate at the temperature of the air; the solid residue of this evaporation was variable in amount, and consisted principally of acetylphenylthiocarbamide. In the precipitate, which was sometimes oily and sometimes granular, aniline thiocyanate and acetanilide were found, together with more or less acetylphenylthiocarbamide. When operating at temperatures higher than 20°, the constituents were heated separately to the initial temperature of the experiment and then mixed; where it was desired to work at the highest temperatures attainable in open vessels, with benzene or toluene as solvent, one constituent was boiled in a reflux apparatus, while the other was allowed to drip in slowly from a tap-funnel; in such preparations, only one molecular proportion of base was employed for each molecular proportion of acetyl chloride taken, a further charge being added subsequently to the warm mixture if any odour of thiocyanate could be detected. Usually, in these cases, little or no precipitate appeared until the solutions were concentrated by spontaneous evaporation at the ordinary temperature; it may here be mentioned incidentally, that if a mixture of aniline thiocyanate with much benzene is heated on the water-bath sufficiently to drive off all the benzene, isomeric change into phenylthiourea occurs to a very perceptible extent.

Without going into details concerning the results of individual experiments, the conclusions to which they lead may be stated, qualitatively and quantitatively, so far as these experiments have been carried, in the following way.

Acetyl thiocyanate, when interacting with aniline, produces always more or less acetylphenylthiocarbamide, and hence does not act exclusively as thiocyanate; neither does it behave purely as a thiocarbamide, for the products have never yet been found quite free from aniline thiocyanate. Two processes, in fact, appear to take place simultaneously:

(i) An additive-compound is formed, thus:

$$AcNCS + PhNH_2 = AcNH{\cdot}CS{\cdot}NHPh.$$

(ii) Double decomposition occurs, according to the equations:

$$(a)\ AcSCN + PhNH_2 = PhNHAc + HSCN, \text{ and}$$
$$(b)\ HSCN + PhNH_2 = PhNH_2,HSCN.$$

If the temperature of interaction is kept very low, process (i) is almost in abeyance, the action occurring as in (ii), but with rising temperature this kind of change becomes less and less marked, until, in boiling benzene, over nine-tenths of the weight of acetyl compound present unites additively with the aniline, as shown by equation (i), to form the disubstituted thiocarbamide.

Of the three products, namely, aniline thiocyanate, acetanilide, and acetylphenylthiocarbamide, the first is nearly insoluble in benzene, the second is but sparingly soluble in the cold, the third dissolves to a moderate extent; in those cases where aniline caused direct precipitation, the benzene mother liquor was evaporated to dryness and the residue, if trifling, accounted as thiocarbamide; but if it amounted to several grams, the acetanilide was removed by crystallising from dilute alcohol, in which the thiocarbimide is but sparingly soluble at the ordinary temperature. To separate the constituents of the precipitate which formed in the benzene solution when aniline was added, the dry mixture was treated with cold water until free from aniline thiocyanate; the aqueous extract, when evaporated to dryness, left a residue, which was weighed and considered to be the aniline thiocyanate originally present. In some experiments, the residue left after extraction of the aniline thiocyanate was dried and weighed again, the difference between the two weighings being taken as a measure of the aniline thiccyanate. Finally, the residue was dissolved in boiling dilute alcohol, from which, on cooling, most of the thiocarbamide crystallised out, and was weighed directly; the acetanilide was determined, sometimes by difference and sometimes by evaporating to a small bulk the weak alcoholic solution from which the thiocarbamide had been deposited, and collecting the anilide which separated out, the latter method being preferred, since, by determining the melting point of the product, it could be ascertained whether the anilide was tolerably pure.

It need scarcely be said that the methods employed, especially those for the quantitative determination of the products, are capable of yielding only very rough approximations to the actual values, more particularly as regards the proportion of acetylphenylthiocarbamide, a value which it was important to secure. But the investigation, so far as it had gone, amounted to little more than a series of preliminary

experiments, in which no greater accuracy was contemplated than would suffice to indicate broadly the course of the interactions. In such a series, no special precautions were taken to secure uniformity; the acetyl chloride was used as purchased, and contained phosphorus, the aniline was not freshly distilled, variable weights of materials were employed for interaction, and the degree of dilution of the materials with benzene was not measured. Naturally, therefore, the results present certain discrepancies in detail, but not such as to obscure the main issue.

The following experiments are arranged, not in the order of their performance, but according to the temperatures at which the constituents were mixed. Moreover, the quantities of acetyl thiocyanate named are calculated (save where the pure substance was employed) from the weight of acetyl chloride taken, assuming a quantitative exchange of chlorine for the thiocyanogen group.

No. 1.—Temperature of interaction from $-8°$ to $-3°$: 5·05 grams of pure freshly distilled acetyl thiocyanate and 9·3 grams of aniline yielded 13·5 grams of solid matter; the mother liquor, free from thiocyanic acid, gave 0·5 gram of acetylphenylthiocarbamide, the total weight being 14 grams. The precipitate, which appeared to consist entirely of acetanilide and aniline thiocyanate, gave on treatment with water 6 grams of acetanilide, against 6·45 calculated, after allowing for the amount of thiocarbamide obtained; this leaves 7·5 for the aniline thiocyanate, but on evaporating the solution only 5 grams of solid were left. The weight of acetylphenylthiocarbamide corresponds to 5·2 per cent. of what the acetyl compound could yield if acting exclusively as thiocarbimide.

No. 2.—Temperature, $-5°$ to $-2°$: 5·05 grams of acetyl thiocyanate in much benzene and 9·3 grams of aniline yielded very little solid, the product being mainly oil. In all, 9·7 grams were obtained, together with 1·5 grams from the mother liquor, the whole containing 1·3 grams of acetylphenylthiocarbamide (m. p. 171—172°). The 9·7 grams of precipitate were resolved by cold water into 4·5 grams of residue, whilst 4·5 grams were left on evaporating the aqueous extract; 0·7 gram, therefore, remains unaccounted for in this process. Acetylphenylthiocarbamide (1·3 grams) would absorb 0·675 gram of acetyl thiocyanate, leaving 4·325 grams to behave as acetylthiocarbimide; this should give 12·3 grams of mixture, whereas 9·7 grams only were obtained. Assuming this mixture to consist solely of thiocyanate and anilide, the latter would amount to about 4·56 grams, whilst, as stated above, 4·5 grams of crude acetanilide were left. The weight of acetylphenylthiocarbamide produced corresponds to about 13·5 per cent. of what could result if the yield of the acetyl compound were quantitative and its function purely thiocarbimidic (this is called below the

"possible yield"), and the total weight of products accounts for 81 per cent. of the acetyl chloride used.

No. 3.—Temperature, $-6°$ to $+1°$ (mean about $-2°$): 10·1 grams of acetylthiocyanate and 18·6 grams of aniline yielded 20 grams of solid matter, and 3 grams of acetylphenylthiocarbamide were found in the mother liquor. When extracted with cold water, the main crop left 7 grams of acetanilide not quite free from thiocarbamide, and the extract gave 13 grams of residue, mostly aniline thiocyanate. This salt cannot be evaporated to dryness in aqueous solution without undergoing some change into phenylthiourea. Reckoned as in the preceding experiment, the yield of acetylphenylthiocarbamide amounts to about 15·5 per cent. of that possible, and the total weight of products accounts for some 85 per cent. of the acetyl chloride employed.

No. 4.—Temperature, 20°, rising to 55° (mean about 37°): 5·05 grams of acetylthiocyanate and 7·65 grams of aniline gave 3·2 grams of acetylphenylthiocarbamide, or about 33 per cent. of the possible yield; in addition, there were 2 grams of acetanilide and 2·5 grams of aniline thiocyanate. These products would absorb in their formation 1·66 grams of acetyl thiocyanate and 0·75 and 0·83 gram respectively of acetylthiocarbimide, the total, 3·24 grams, corresponding to 68 per cent. of the acetyl chloride taken.

No. 5.—Temperature, 40° to 50° (mean about 45°): 10·1 grams of acetyl thiocyanate and 14·3 grams of aniline yielded 9 grams of acetylphenylthiocarbamide, corresponding to 46·5 per cent. of the possible yield, and absorbing 4·68 grams of acetylthiocarbimide; in addition, there were 13 grams of mixed anilide and thiocyanate, thereby accounting for 92 per cent. of the acetyl chloride used.

No. 6.—Temperature, 50° to 85° (mean about 67°): 5·05 grams of acetyl thiocyanate and 5·65 grams of aniline. On bringing the constituents together, the temperature rose quickly to 85°, whereupon the mixture began to boil. A solid mixture (10·5 grams) was obtained, which gave up to cold water 2·5 grams of aniline thiocyanate; the remaining 8 grams were resolved into 4 grams of pure recrystallised acetylphenylthiocarbamide and 2 grams of acetanilide. Since the 2·5 grams of thiocyanate would be accompanied by 2·8 grams of acetanilide, the 4 grams of recrystallised thiocarbamide came, presumably, from 5·2 grams originally present in the mixture. That is, 53·5 per cent. of the acetyl compound, supposing it to be formed quantitatively, has acted as thiocarbimide; the remainder, acting as thiocyanate, should give 6·65 grams of mixed anilide and thiocyanate, or a total of 11·85 grams against the 10·5 grams obtained. Hence, in this experiment, of the acetyl chloride employed, about 89 per cent. is accounted for.

No. 7.—10·1 grams of acetyl thiocyanate and 9·3 grams of aniline, both dissolved in benzene, were heated separately to 75° and the solutions mixed in bulk; the mixture boiled freely, but nothing separated, except a trace of oily matter. The solution, when poured off from this and left, slowly deposited 10 grams of practically pure acetylphenylthiocarbamide (m. p. 171—172°); the mother liquor required 3 grams more of aniline to destroy the odour of acetyl thiocyanate, and by evaporation gave 8·5 grams of a solid containing very little thiocarbamide, but giving distinctly the reactions of aniline thiocyanate. The yield of acetylphenylthiocarbamide amounts to 41·5 per cent. of that possible, whilst 77·5 per cent. of the acetyl chloride taken is accounted for in the total weight of products obtained.

The three following experiments were conducted by allowing the acetyl compound to drip slowly down a tube, passing through a vertical condenser into a boiling solution of the amine, or *vice versâ*; the temperatures were not measured, but where benzene was employed as solvent were probably not very far from 85°.

No. 8.—10·1 grams of acetyl thiocyanate in benzene were passed slowly into a boiling solution of 9·3 grams of aniline in benzene; on cooling, 11 grams of thiocarbamide crystallised out, and the mother liquor, when concentrated, gave 6 grams more of the same substance, the total amounting to about 88 per cent. of the possible yield.

No. 9.—The preceding experiment was repeated under identical conditions, except that the amine was dropped into the solution of the thiocyanate and the mixture effected more rapidly: 15·5 grams of acetylphenylthiocarbamide resulted, or about 80 per cent. of the possible yield; in both this and the preceding experiment, the mother liquor gave marked indications of thiocyanic acid.

No. 10.—5·05 grams of acetyl thiocyanate were used, the solution of the amine (4·65 grams) being admitted below the surface of the boiling liquid; in this way, 8·8 grams of thiocarbamide were obtained, or about 91 per cent. of the possible quantity.

No. 11.—5·05 grams of pure distilled thiocyanate and 4·7 grams of aniline, each dissolved separately in boiling toluene, were mixed quickly; the interaction was very vigorous, and ultimately 8 grams of acetylphenylthiocarbamide were collected, amounting to only 82·5 per cent. of the possible yield. The mother liquor reacted very freely for thiocyanic acid.

In certain of the experiments described above, the change of temperature during the interaction was so large compared with the total range brought under observation that it is difficult to connect yield and temperature save in an approximate manner, which does not admit of the results being plotted as a curve. Moreover, even if the

temperatures were known within a few degrees for each interaction, it is doubtful whether the methods adopted for measuring the yields of the various products are sufficiently precise to define its shape. Nevertheless, it is easy enough to follow in a general way the effect produced by increasing temperature on the power exhibited by acetyl thiocyanate of affording a thiocarbamide with aniline; unfortunately, the determinations of the relative quantity of thiocyanic acid formed, also an important factor, are too few and too erratic to lend themselves to tabulation.

As a basis for the figures given in the following table, the method of calculation adopted is this: (i) where the temperature varied much during interaction, the mean value is taken; in cases where boiling occurred, the temperature thereby attained is taken as 85°; (ii) it is assumed that the whole of the acetyl chloride employed in any experiment is converted into the corresponding thiocyanate, and that the latter is collected without loss; (iii) the weight of acetylphenylthiocarbamide obtained is taken as the measure of the quantity of acetylthiocarbimide present at a given temperature, the percentage of acetylthiocarbimide being calculated on the principle that a yield of 194 parts of thiocarbamide for 78·5 parts of acetyl chloride employed would correspond to 100 per cent. of acetylthiocarbimide existing in the "thiocyanate." Experiments 9 and 11 have not been incorporated in the table, the former being omitted because the usual order of mixing the constituents was reversed, and the latter because a different solvent was employed.

Table showing the Effect of Temperature on the Interaction between Aniline and Acetyl Thiocyanate.

No. of experiment.	Mean temperature of interaction.	Percentage of acetyl thiocarbimide.	No. of experiment.	Mean temperature of interaction.	Percentage of acetyl thiocarbimide.
1	−5°	5·2	6	+67°	53·7
2	−4	13·4	7	+80 (?)	51·5
3	−2	15·5	8	B.p. of benzene solution	87·7
4	+37	33·0	10	B.p. of benzene solution	91·0
5	+45	46·5			

Acetyl Thiocyanate and other Bases.

(*a*) o-*Toluidine.*

Two experiments were carried out in benzene solution.

(i) 5·05 grams of acetyl thiocyanate were added slowly to 10·7 grams of *o*-toluidine at about −3°. Solid and oil were formed, the latter being separated as far as possible at the pump; the residue, a sticky mass weighing 9 grams, when recrystallised from spirit, gave 6 grams of acetyl-*o*-tolylthiocarbamide, melting at 183—184°.

(ii) This process was repeated at the boiling point with 5·05 grams of acetyl thiocyanate and 5·5 grams of amine; 9·5 grams of crystalline solid resulted, and the mother liquor gave 0·3 gram more, together with some oily droplets, reacting strongly for thiocyanic acid. On recrystallisation, the main crop gave 8·5 grams of acetyl-*o*-tolylthiocarbamide (m. p. 184°).

So far as can be judged from these experiments, temperature has little influence, if any, between the limits indicated, on the combination between *o*-toluidine and acetylthiocarbimide, the yields of additive product amounting respectively to 86·5 and more than 91 per cent. of that theoretically possible; the slight deficiency in the former case may perhaps be due to the solvent action of a quantity of uncombined *o*-toluidine.

(*b*) *Secondary Bases.*

(i) *Methylaniline.*—Concurrently with the foregoing experiments, attempts were made to combine acetyl thiocyanate with some secondary bases; the first of these selected was methylaniline. Vigorous interaction occurred on mixing the constituents in benzene solution, heated nearly to the boiling point; the mixture on cooling deposited white crystals amounting to about 36 per cent. of the possible yield. When recrystallised from dilute alcohol, the product melted at 93—94° with decomposition, and afforded 15·56 per cent. of sulphur against 15·4 calculated for $C_{10}H_{12}ON_2S$. Acetylmethylphenylthiourea dissolves very freely in alcohol and in benzene, and is desulphurised by alkaline lead solution only after prolonged boiling.

(ii) *Benzylaniline.*—Combination was less energetic than in the preceding case, but the yield was very satisfactory, amounting to more than 91 per cent. of that theoretically possible. When recrystallised from weak spirit, the substance formed a mass of fine rhombic crystals melting at 110—111°.

Found, S = 11·23; $C_{16}H_{16}ON_2S$ requires S = 11·26 per cent.

Acetylphenylbenzylthiourea is readily soluble in hot alcohol or benzene, moderately so in cold; it is insoluble in water, and nearly insoluble in light petroleum.

(iii) *Piperidine.*—With this base, somewhat singular results were obtained, of which a satisfactory explanation is still wanting.

Piperidine (8·5 grams), dissolved in benzene, was dropped slowly into a boiling benzene solution of 10·1 grams of acetyl thiocyanate; very vigorous action occurred, and even while the liquid was still hot a solid separated in large, shining plates. On cooling, this product was collected; its weight amounted to 2 grams, and the substance, when recrystallised from chloroform, melted at 95—96° and proved

to be piperidine thiocyanate. The mother liquor reacted strongly for thiocyanic acid, and was freely desulphurised by alkaline lead or silver salts, but no sign of solid matter was observed in the viscid residue, even after very prolonged standing. After several months, the residue was mixed with alcohol, whereupon the odour of ethyl acetate soon became distinctly perceptible, increasing gradually to a maximum and then slowly passing off; meanwhile, very fine large crystals began to be deposited, of which, after a few weeks, two grams were obtained; they melted, both before and after recrystallisation, from a mixture of alcohol with benzene at 126—127°, but proved not to be the expected acetylpiperidylthiourea.

The product exhibited the general properties of a thiourea, being readily desulphurised, for instance, by ammoniacal silver nitrate even in the cold; but an analysis gave S = 22·1, whilst the compound $AcN{\cdot}C(SH){\cdot}NC_5H_{10}$ would require S = 17·21 per cent. But the properties, the melting point, and the amount of contained sulphur are all consistent with the view that the substance is identical with the "piperidylthiourea" obtained by Wallach (*Ber.*, 1899, **32**, 1872) from cyanogen bromide, piperidine, and hydrogen sulphide. The experiment was twice repeated with precisely similar results; in one case, every precaution was taken against access of moisture and a slightly increased quantity of the amine was used; no difference whatever was observed in the course of the process, but ultimately larger yields of piperidine thiocyanate and the thiourea were obtained, amounting to 3·2 grams of the former and 4·0 grams of the latter, reckoned on the same quantity of acetyl thiocyanate as before.

Assuming that acetylpiperidylthiourea is first formed, a possible explanation of the production of piperidylthiourea is the following:

$$AcNH{\cdot}C(SH){\cdot}NC_5H_{10} + EtOH = EtOAc + NH_2{\cdot}C(SH){\cdot}NC_5H_{10}.$$

Two difficulties, however, stand in the way of its acceptance. The first is that, as a rule, trisubstituted thioureas are not very easily saponified, and therefore it is scarcely credible that cold alcohol should be able to remove the acetyl group; on the other hand, piperidylthiourea is formed with exceptional difficulty by the ordinary method,* and hence the acetyl derivative might conceivably present features differing from those of other compounds of this class. However, acetylpiperidylthiourea can be prepared by the direct acetylation of this supposed piperidylthiourea, and its properties constitute the second difficulty as regards the suggested explanation.

On warming the supposed piperidylthiourea on the water-bath with excess of acetic anhydride, it soon dissolved, and crystals separated on

* The compiler has made several unsuccessful attempts to convert piperidine thiocyanate, by heating, into the isomeric thiourea.

cooling; when recrystallised from boiling water, they formed long prisms, easily distinguishable from the short, thick crystals of the parent substance, and melting at 112—113°. The new compound dissolves freely in alcohol or benzene; it is easily soluble in hot water, but sparingly in the cold solvent, and is nearly insoluble in light petroleum. Moreover, the acetyl group is very firmly held, for the solution was not desulphurised by ordinary treatment with alkaline salts of lead or silver, but yielded up its sulphur only after boiling with concentrated potassium hydroxide. A sulphur determination gave 17·3, the number calculated for $C_8H_{14}ON_2S$ being 17·21 per cent.

When boiled with alcohol, not a trace of ethyl acetate was formed; it is therefore certain that the piperidylthiourea resulting as described above does not originate through the action of alcohol on the acetylpiperidylthiourea already formed.

(*c*) *Ammonia.*

In almost every case hitherto recorded where ammonia interacts with the thiocyanate of a fatty acid, little or no thiourea is formed, but the products of double decomposition, namely, thiocyanic acid, together with fatty amide appear instead. The first experiment of this kind was carried out by Miquel, who obtained from his acetyl thiocyanate an oil, miscible with water and having the empirical composition of acetamide thiocyanate; from this oil, a very small quantity of a crystalline solid was deposited, which he conjectured might possibly be acetylthiourea.

Since the power of acetyl thiocyanate to combine directly with aniline is so greatly enhanced at high temperatures, the question naturally arose whether this might also be favourable to its union with ammonia. In order to decide this point, ammonia gas (not dried) was led through a solution of the acetyl compound in boiling benzene; much fuming occurred, with separation of an oil which proved to be ammonium thiocyanate, and the liquor poured off from this deposited a small quantity of nearly pure acetylthiourea. On repeating the experiment with 8 grams of freshly distilled acetyl thiocyanate in boiling toluene, a little oil separated, which presently crystallised (ammonium thiocyanate); some hydrogen sulphide escaped, and from the residual liquor 2 grams of acetylthiourea were obtained, or a little more than 21 per cent. of the possible yield, supposing the acetyl compound to be purely thiocarbimidic in function.

The above results, although not decisive, seem to point in the same direction as those obtained with aniline.

This concludes the work carried out by the author (R. E. D.) on acetyl thiocyanate.

PART II.

Carboxyphenyl- and Carboxyguaiacol-thiocarbamides.

The following preliminary experiments were carried out with the assistance of samples of the chlorocarbonates derived from phenol and from guaiacol, which had kindly been presented to the author by the Farbenfabriken vorm. F. Bayer & Co.

In order to prepare carboxyphenylthiocarbimide, phenyl chlorocarbonate, $C_6H_5O{\cdot}COCl$, dissolved in benzene, was left for some days in contact with finely powdered dry potassium thiocyanate until the solution ceased to give the reactions of chlorine; the solid was then removed at the pump and washed with more benzene. The filtrate had little pungent odour, and when shaken up with water afforded no thiocyanic acid, but gave with alkaline solutions of silver and lead salts the desulphurisation reactions indicating the presence of a thiocarbimide, and when treated with bases combined with them, evolving heat and producing the corresponding additive compounds.

Carboxyphenylmethylthiocarbamide, $C_6H_5{\cdot}O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}CH_3$.

By mixing the benzene solution with aqueous methylamine, diluted with alcohol, and allowing the mixture to concentrate by evaporation, a somewhat oily solid was obtained, crystallising from alcohol, which dissolves it moderately easily when hot, but sparingly in the cold, in long, glistening prisms melting at 175—176°.

0·204 gave 0·228 $BaSO_4$. S = 15·36

$C_9H_{10}O_2N_2S$ requires S = 15·27 per cent.

This substance is isomeric with the carboxymethylphenylthiocarbamide, $MeO{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NHPh$ (m. p. 158°), obtained by the author (Trans., 1901, 79, 908) from carboxymethylthiocarbimide and aniline.

*Carboxyphenyl*iso*amylthiocarbamide*, $C_6H_5{\cdot}O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_5H_{11}$.

Using *iso*amylamine, a solid was obtained together with a good deal of oil, the latter being extracted at the pump: the crystalline solid, after washing with dilute alcohol, melted at 99—100° and gave S = 12·05 against S = 12·03 per cent., calculated for $C_{13}H_{18}O_2N_2S$.

Carboxy*iso*amylphenylthiocarbamide, $C_5H_{11}O{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5$ (*loc. cit.*, p. 914), isomeric with the above compound, melts at 97—98°.

Carboxydiphenylthiocarbamide, $C_6H_5 \cdot O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5$.

Aniline gave the diphenylated derivative, which melted at 148—149° and was easily desulphurised by alkaline lead tartrate.

Found, S = 11·78. $C_{14}H_{12}O_2N_2S$ requires S = 11·76 per cent.

Acetylphenylthiocarbamide (2 grams), when warmed on the water-bath with excess of phenyl chlorocarbonate, gradually dissolved, whilst acetyl chloride escaped, and the resultant mixture, when cooled and treated with alcohol, yielded the above carboxydiphenyl compound (1·5 grams), melting at 148—149° :

$$PhCO_2Cl + AcNH \cdot CS \cdot NHPh = AcCl + PhO \cdot CO \cdot NH \cdot CS \cdot NHPh.$$

Carboxyguaiacolphenylthiocarbamide,
$CH_3 \cdot O \cdot C_6H_4 \cdot O \cdot CO \cdot NH \cdot CS \cdot NH \cdot C_6H_5$.

This compound, like the preceding, was obtained by expelling the acetyl group from acetylphenylthiocarbamide, guaiacol chlorocarbonate being employed for the purpose. A solid was obtained, melting at 154—155° and giving a fine mirror of galena when warmed with an alkaline solution of lead tartrate.

The composition was checked by means of a sulphur determination :

0·208 gave 0·159 gram $BaSO_4$. S = 10·5.
$C_{15}H_{14}O_3N_2S$ requires S = 10·59 per cent.

By treating with alcoholic ammonia the solution containing the product of the action of phenyl chlorocarbonate on potassium thiocyanate, a solid was obtained melting at 169—170°; it was desulphurised at once in the cold by ammoniacal silver nitrate, and slowly on boiling with an alkaline lead solution. No analysis was made, but in view of the mode of preparation and the properties mentioned, there can be little doubt that this substance was carboxyphenylthiourea.

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XLI.—*Pinene* iso*Nitrosocyanide and its Derivatives.

By William Augustus Tilden and Harry Burrows.

A brief description of the cyanide and some of its reactions has been given in the "Preliminary notice of some new derivatives of pinene and other terpenes," by the same authors (Proc., 1902, **18**, 161).

Pinene iso*Nitrosocyanide.*—In order to prepare this compound, a number of flasks are each charged with 20 grams of pinene nitrosochloride, 8 grams of finely-powdered potassium cyanide, and 75 c.c. of alcohol (84 per cent.), and the mixture left at the ordinary temperature with frequent shaking for at least twenty-four hours. Eight grams of cyanide and 30 c.c. of alcohol are then added, and the mixture slowly heated to the boiling point and kept at that temperature until the reaction is finished. Sufficient heat is developed to keep the alcohol boiling for a few minutes. The mixture is then poured into about six times its volume of cold water and left for a few hours. The nitrosocyanide is precipitated, and may be purified by crystallisation from alcohol. The nitrosochloride yields rather less than half its weight of the cyanide. The by-products are viscid and do not crystallise even after long standing.

This compound crystallises in thick, colourless prisms which melt at 171°. When crystallised from ether and occasionally from other solvents, it readily yields large, transparent prisms, which exhibit triboluminescence in a remarkable degree. On decanting the mother liquor from the crystals, flashes of light accompanied by a crackling sound were several times noticed. These phenomena seem to be dependent on the size and transparency of the crystals. The opaque crystals which are often formed give no flash when crushed.

This nitrosocyanide is soluble in dilute alkali, and is unchanged by boiling with a concentrated solution of caustic potash, being precipitated unaltered on addition of an acid. Boiled with dilute hydrochloric acid, it yields hydroxylamine and uncrystallisable products. It behaves as a saturated compound towards bromine, and is not oxidised by alkaline permanganate. The nitrosocyanide and its derivatives are optically inactive.

0·1948 gave 0·4916 CO_2 and 0·1436 H_2O. C = 68·83 ; H = 8·19.
0·2220 ,, 28·4 c.c. moist nitrogen at 24° and 766 mm. N = 14·47.
$C_{11}H_{16}ON_2$ requires C = 68·75 ; H = 8·33 ; N = 14·58 per cent.

Dissolved in benzene, it gave by the cryoscopic method a molecular weight 188, whilst the formula $C_{10}H_{15}(\dot{:}NOH)\cdot CN$ corresponds with 192.

The only compound of the kind which appears to have been investigated is the cyanide obtained by Wallach from amylene nitrosate (*Annalen*, 1888, **248**, 164). That compound is, however, fairly easily hydrolysed by caustic potash, yielding the corresponding amide and acid. This difference of behaviour can only be attributed to the difference of constitution of the parent hydrocarbons, amylene being an open chain, whilst pinene has a cyclic structure. In both compounds, the oxime and nitrile groups are in the ortho position relatively to each other.

Methyl Ether of Pinene iso*Nitrosocyanide.*—Five grams of pinene *iso*-nitrosocyanide, 2 grams of caustic soda, and 5 grams of methyl iodide were dissolved in 100 c.c. of methyl alcohol and boiled for six hours. After evaporation of the alcohol, the residue was washed with water and crystallised from petroleum. Large, colourless prisms were obtained melting at 67°.

0·2611 gave 31·4 c.c. moist nitrogen at 19° and 750 mm. N = 13·64.
$C_{12}H_{18}ON_2$ requires N = 13·60 per cent.

Benzoyl Ester.—Treated with benzoyl chloride and caustic soda, the cyanide yields a benzoyl derivative which, after crystallising from alcohol, melts at 102°.

Nitro-compound, $C_{10}H_{15}(NO_2)_2 \cdot CN$.—When pinene *iso*nitrosocyanide is added to a cooled mixture of equal volumes of nitric acid (sp. gr. 1·42) and acetic anhydride, it dissolves with evolution of red fumes, and on diluting with water a compound is precipitated which may be crystallised from a mixture of ether and light petroleum. It melts at 105° with evolution of red fumes. This compound responds to Liebermann's test, but is insoluble in aqueous alkalis. The same compound is produced when gaseous nitrogen peroxide is passed into a cooled solution of the cyanide in chloroform.

0·1187 gave 0·2258 CO_2 and 0·0676 H_2O. C = 51·87 ; H = 6·35.
0·1241 ,, 18·4 c.c. moist nitrogen at 17° and 757 mm. N = 17·07.
$C_{11}H_{15}O_4N_3$ requires C = 52·17 ; H = 5·92 ; N = 16·60 per cent.

Dissolved in benzene, it gave, by the cryoscopic method, the molecular weight 248 : the above formula requires 254.

When the nitro-compound is reduced by zinc and acetic acid or by hydrogen sulphide, the original *iso*nitrosocyanide is reproduced. Reduction by sodium and alcohol leads to the evolution of much ammonia and formation of pinylamine. These reactions appear to indicate that in the formation of this compound the oxime group is oxidised, and that the second nitro-group is attached to the same carbon atom as the first, $:C:N \cdot OH$ becoming $:C<^{NO_2}_{NO_2}$.

Pinene iso*Nitrosocarboxylamide*, $C_{10}H_{15}(:NOH)\cdot CO\cdot NH_2$.—A solution of the cyanide in three to four times its weight of concentrated sulphuric acid, kept at a temperature about 80° for two hours, yields this compound, with little loss, on diluting the acid with water. The mother liquor gives a small additional quantity of the amide, and a small purple precipitate which is soluble in alcohol, forming a bright red solution. The amide crystallised from alcohol yields colourless prisms which melt at 220° with decomposition. The amide is slightly soluble in dilute alkali, but is unaltered by strong boiling caustic soda. It is soluble in concentrated hydrochloric acid, and is partly precipitated unchanged on dilution with water. It is unaffected by bromine or alkaline hypobromite.

I. 0·1132 gave 0·2602 CO_2 and 0·0857 H_2O. C = 62·67 ; H = 8·41.
II. 0·1712 „ 0·3943 CO_2 „ 0·1318 H_2O. C = 62·80 ; H = 8·55.
III. 0·2629 „ 32·6 c.c. moist nitrogen at 24·5° and 767 mm. N = 13·78.
IV. 0·1901 gave 22·7 c.c. moist nitrogen at 24° and 762 mm. N = 13·43.

$C_{11}H_{18}O_2N_2$ requires C = 62·85 ; H = 8·57 ; N = 13·3.

Methyl Ether, $C_{10}H_{15}(:NO\cdot CH_3)\cdot CO\cdot NH_2$.—Prepared in the same manner as the ether of the cyanide, it crystallises from methyl alcohol in large, colourless prisms melting at 145°. The same compound is obtained when the caustic soda in the process is replaced by silver oxide.

0·1230 gave 14·4 c.c. moist nitrogen at 25° and 764 mm. N = 12·6.
$C_{12}H_{20}O_2N_2$ requires N = 12·5 per cent.

Benzoyl Ester, $C_{10}H_{15}(:NO\cdot C_7H_5O)\cdot CO\cdot NH_2$.—This compound was prepared by the aid of benzoyl chloride and caustic soda in the usual manner. It forms colourless crystals which melt at 197°, and on saponification by means of alcoholic soda yield the unaltered amide. The benzoyl compound is incapable of interacting with methyl iodide and silver oxide.

0·1260 gave 10·6 c.c. moist nitrogen at 25° and 764 mm. N = 9·05.
$C_{18}H_{22}O_3N_2$ requires N = 8·91 per cent.

Pinene *iso*nitrosocarboxylic acid corresponding with the amide has not been obtained. When the amide is heated to 100° with about four times its weight of 20 per cent. hydrochloric acid, it dissolves, and after a time a viscid oil separates in considerable quantity. The acid solution evaporated to dryness leaves abundance of ammonium chloride mixed with unchanged amide. On distillation in steam, part of the oil passes over and forms a nearly colourless liquid which floats on

water and is very soluble in alkalis. It contains no nitrogen and appears to consist of the ketonic acid $O:C_{10}H_{15}\cdot CO_2H$, which would result from the hydrolysis of both the amide and oxime groups. No crystalline compounds could be obtained from it, nor would it react with hydroxylamine in alkaline solution. It gives no colour with ferric chloride.

Pinene Carboxylic Amide Pseudoxime or Lactam.—When a solution of the amide in concentrated sulphuric acid is heated to 100° for about six hours, a further change occurs, and the colour of the solution darkens considerably. Care is necessary to avoid any rise of temperature above 100°, otherwise the product is destroyed with evolution of sulphur dioxide. On diluting the liquid with water and neutralising with ammonia, crystals are deposited which, after recrystallisation from alcohol, melt at 209°. This compound has the same composition as the amide, together with a molecule of water of crystallisation. It is insoluble in cold alkali, but on boiling with concentrated solution of caustic soda it gradually dissolves, while ammonia is evolved. It gives no methyl derivative.

I. 0·1274 gave 0·2672 CO_2 and 0·1014 H_2O. C = 57·3 ; H = 8·86.
II. 0·1670 ,, 0·3564 CO_2 ,, 0·1304 H_2O. C = 58·2 ; H = 8·67.
III. 0·1572 ,, 17 c.c. moist nitrogen at 16° and 769 mm. N = 12·75.
IV. 0·1736 at 110° lost 0·0142, and 0·2294 at 110° lost 0·0186. H_2O = 8·1 and 8·1.
$C_{11}H_{18}O_2N_2,H_2O$ requires C = 57·9 ; H = 8·7 ; N = 12·28 ; H_2O = 7·9 per cent.

Pinene Carboxylic Acid Pseudoxime or Lactam.—This compound is obtained by boiling the amide just described with concentrated aqueous solution of caustic soda till evolution of ammonia ceases, then neutralising with hydrochloric acid. The acid recrystallised from alcohol forms small, colourless prisms which contain water of crystallisation and melt at 220°. Its alkali salts are very soluble in water.

The acid does not react with hydroxylamine in alkaline solution.

I. 0·2012 heated at 110° lost 0·0156. H_2O = 7·75.
II. 0·1850 gave 0·3870 CO_2 and 0·1373 H_2O. C = 57·05 ; H = 8·25.
III. 0·1059 ,, 0·2210 CO_2 ,, 0·0796 H_2O. C = 56·92 ; H = 8·35.
IV. 0·1678 ,, 9·0 c.c. moist nitrogen at 18° and 765 mm. N = 6·24.
$C_{11}H_{17}O_3N,H_2O$ requires H_2O = 7·86; C = 57·6; H = 8·29; N = 6·11 per cent.

0·4829 titrated with $N/10$ caustic soda required for its neutralisation 20 c.c., corresponding with 0·800 NaHO, instead of 0·843 as required by theory.

Salts.—The acid suspended in absolute alcohol and saturated with

ammonia gas dissolves, and the solution by spontaneous evaporation leaves flat prisms of the ammonium salt. The ammonium salt, dissolved in water and mixed with the calculated amount of silver nitrate, gives the silver salt as a white, crystalline precipitate which is somewhat sensitive to light.

0·3214 gave on heating 0·1088 of silver corresponding with 33·85 per cent. : $C_{11}H_{16}O_3NAg$ requires Ag = 33·96.

The methyl ester was prepared from the silver salt by action of methyl iodide diluted with ether. It melts at 132°.

0·1190 gave 6·8 c.c. moist nitrogen at 23° and 756 mm. N = 6·37.
$C_{12}H_{19}O_3N$ requires N = 6·22 per cent.

When the acid is heated to about 120° with 20 per cent. hydrochloric acid, a colourless solution is formed, which, on evaporation to dryness, gives a white, crystalline residue soluble in water. No gas is evolved on opening the tube. The compound crystallises from water in long prisms, and was found to consist of the hydrochloride of an amino-acid.

After drying at 100°, the crystals, by direct titration with silver nitrate, were found to contain 13·64 per cent. of chlorine. The formula $C_{11}H_{19}O_4N,HCl$ requires Cl = 13·37 per cent.

An attempt to obtain this compound by heating the amide, instead of the acid, with hydrochloric acid failed, as only uncrystallisable products were formed. This amino-acid is now undergoing investigation.

Theoretical.

Pinene being represented by the following expression,

$$(C_6H_{10})''\!\!<\!\!\begin{array}{l}\text{——}\overset{\displaystyle CH_3}{\overset{|}{C}}\\ \quad\; CH_2\cdot\overset{||}{C}H\end{array},$$

the nitrosochloride and compounds derived from it may be represented by the following formulæ:

Nitrosochloride (bimolecular), $\begin{array}{l}\text{——}\overset{\displaystyle CH_3}{\overset{|}{C}}Cl\\ -CH_2\cdot\overset{|}{C}H\cdot NO\end{array}$.

*iso*Nitrosocyanide (m. p. 171°, unimolecular), $\begin{array}{l}\text{——}\overset{\displaystyle CH_3}{\overset{|}{C}}\cdot CN\\ -CH_2\cdot\overset{|}{C}:NOH\end{array}$.

Amide (m. p. 220°), $\begin{array}{l}\text{——}\overset{\displaystyle CH_3}{\overset{|}{C}}\cdot CO\cdot NH_2\\ -CH_2\cdot\overset{|}{C}:NOH\end{array}$.

Ketonic acid (oil),

$$\begin{array}{l} \quad\quad CH_3 \\ \quad\quad | \\ \text{——}C{\cdot}CO_2H \, . \\ \quad\quad | \\ -CH_2{\cdot}CO \end{array}$$

Amide pseudoxime (m. p. 209°),

$$\begin{array}{l} \quad\quad CH_3 \\ \quad\quad | \\ \text{——}C{\cdot}CO{\cdot}NH_2 \\ \quad\quad | \\ \quad\quad NH \\ \quad\quad | \\ -CH_2{\cdot}CO \end{array} \quad \text{or} \quad \begin{array}{l} \quad\quad CH_3 \\ \quad\quad | \\ \text{——}C{\cdot}CO{\cdot}NH_2 \\ \quad\quad | \\ \quad\quad CO \\ \quad\quad | \\ -CH_2{\cdot}NH \end{array} \, .$$

Acid pseudoxime (m. p. 220°),

$$\begin{array}{l} \quad\quad CH_3 \\ \quad\quad | \\ \text{——}C{\cdot}CO_2H \\ \quad\quad | \\ \quad\quad NH \\ \quad\quad | \\ -CH_2{\cdot}CO \end{array} \quad \text{or} \quad \begin{array}{l} \quad\quad CH_3 \\ \quad\quad | \\ \text{——}C{\cdot}CO_2H \\ \quad\quad | \\ \quad\quad CO \\ \quad\quad | \\ -CH_2{\cdot}NH \end{array}$$

The amino-acid is derived therefrom by opening the ring, thus :

$$C_6H_{10}\left\langle \begin{array}{l} CH_3 \\ | \\ C{\cdot}CO_2H \\ | \\ NH_2 \\ CH_2{\cdot}CO_2H \end{array} \right. \quad \text{or} \quad C_6H_{10}\left\langle \begin{array}{l} CH_3 \\ | \\ C{\cdot}CO_2H \\ | \\ CO_2H \\ CH_2{\cdot}NH_2 \end{array} \right. \, .$$

It is hoped that the further study of the products of this change may throw light on the constitution of pinene.

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XLII.—*Gynocardin, a New Cyanogenetic Glucoside.*

By FREDERICK BELDING POWER and FREDERIC HERBERT LEES.

IN a preliminary note it was recorded by one of us and F. H. Gornall (Proc., 1904, **20**, 137) that when the seeds of *Gynocardia odorata* (R. Br.) were crushed and brought into contact with water, a strong odour of hydrogen cyanide was developed, and this behaviour was shown to be due to the presence of a cyanogenetic glucoside, which was isolated and designated *gynocardin*. Since then we have been able to procure a large quantity of gynocardia seeds, which were specially collected for us in India, and have succeeded in isolating gynocardin in a pure state and in an amount sufficient to admit of its further study. The yield of this substance was equal to 5 per cent. of the weight of the seeds.

Gynocardin crystallises from water in colourless, glistening, prismatic needles containing $1\frac{1}{2}$ molecules of water of crystallisation, with which it readily parts at a temperature of 115°. The anhydrous substance melts at 162—163° with only slight decomposition, and has the formula $C_{13}H_{19}O_9N$. It is dextrorotatory, the anhydrous substance having in aqueous solution the specific rotatory power $[\alpha]_D^{21°} + 72·5°$. Definite proof of the cyanogenetic nature of gynocardin is afforded by the fact that when the enzyme of the seeds, *gynocardase*, is brought into its aqueous solution, hydrogen cyanide is quickly evolved.

Until recently, the only definite cyanogenetic glucoside known was amygdalin, $C_{20}H_{27}O_{11}N$, which has the constitution

$$C_{12}H_{21}O_{10}·O·CH(C_6H_5)·CN,$$

and is the maltose ether of benzaldehydecyanohydrin, but, in a series of researches entitled "Cyanogenesis in Plants," Dunstan and Henry have isolated and studied three other definite members of this class. They are lotusin, $C_{28}H_{31}O_{16}N$, the lotoflavin ether of maltosecyano-

O OH

hydrin, $C_{11}H_{21}O_{10}·CH·O·$ [ring structure] OH (*Phil. Trans.*, 1901,

CN

OH CO

194, 515); dhurrin, $C_{14}H_{17}O_7N$, the dextrose ether of *p*-hydroxybenzaldehydecyanohydrin, $C_6H_{11}O_5·O·CH(CN)·C_6H_4·OH$ (*Phil. Trans.*, 1902, **199**, 399); and phaseolunatin, $C_{10}H_{17}O_6N$, the dextrose ether of acetonecyanohydrin, $C_6H_{11}O_5·O·C(CH_3)_2·CN$ (*Proc. Roy. Soc.*, 1903, **72**, 285). It is seen that whereas, on the one hand, amygdalin, dhurrin, and phaseolunatin are sugar ethers of the cyanohydrins of substances other than sugars, lotusin, on the other hand, is an aromatic ether of a sugar cyanohydrin.

The constitution of gynocardin, the fifth member of the class of cyanogenetic glucosides which has been isolated in a pure condition, being thought of some interest, the elucidation of the question has been attempted.

When gynocardin is treated with acetic anhydride and sodium acetate, *hepta-acetylgynocardin*, $C_{13}H_{12}O_9(C_2H_3O)_7N$, is formed; it crystallises in needles melting at 118—119° and has $[\alpha]_D + 40·4°$ in chloroform.

A most remarkable property of gynocardin, which brings it into sharp contrast with the other members of its class, is its great stability towards the usual acid hydrolysing agents. Dhurrin, for example, after heating for five minutes with dilute acid, afforded *p*-hydroxybenzaldehyde on extracting with ether, whereas with gynocardin practically no hydrolysis had taken place on heating for half an hour

with 5 per cent. hydrochloric acid, and complete hydrolysis was not effected until the solution had been heated for 9 hours. During the hydrolysis, hydrogen cyanide is generated, and the solution continually becomes darker in colour, being ultimately dark brown. Among the products of the reaction, it has been possible to identify only *d*-glucose and hydrogen cyanide, although, excluding the contingency of secondary decomposition, which undoubtedly occurs, it should have been possible to obtain, in addition to the above hydrolytic products, a substance of the formula $C_6H_8O_4$, in accordance with the equation :

$$C_{13}H_{19}O_9N + H_2O = C_6H_{12}O_6 + C_6H_8O_4 + HCN.$$

In view of the above-mentioned secondary decomposition, which was thought to be due solely to the prolonged heating necessary to effect hydrolysis, the enzyme, gynocardase, appeared to be better adapted for this purpose. Gynocardin is very readily hydrolysed at the ordinary temperature by the enzyme, but, as in the case of the hydrolysis by acid, the reaction is attended with the formation of dark-coloured resinous matter, and only glucose and hydrogen cyanide could be identified among the products.

Gynocardin readily reacts with hot barium hydroxide, with the liberation of ammonia and the formation of *barium gynocardinate*, $(C_{12}H_{19}O_9 \cdot CO_2)_2Ba$, according to the equation :

$$C_{13}H_{19}O_9N + 2H_2O = C_{12}H_{19}O_9 \cdot CO_2H + NH_3.$$

Gynocardinic acid, $C_{12}H_{19}O_9 \cdot CO_2H$, prepared from its barium salt, is extremely soluble in water, and was only obtained as a nearly colourless syrup ; it is dextrorotatory, and does not reduce Fehling's solution.

When gynocardinic acid is heated with dilute sulphuric acid, it is hydrolysed in accordance with the equation :

$$C_{12}H_{19}O_9 \cdot CO_2H + H_2O = C_6H_{12}O_6 + C_6H_9O_4 \cdot CO_2H.$$

There are formed, *d*-glucose (phenylglucosazone, m. p. 205—206°) and an *acid*, which must have the formula $C_7H_{10}O_6$. This acid could not be separated in a free state from the sugar which accompanied it, but by conveiting it into its *quinine salt* a small amount of the latter could be isolated in a state of purity. This salt formed needles, melting at 224° with decomposition, and on analysis gave numbers agreeing fairly well with the formula $C_{20}H_{24}O_2N_2,C_7H_{10}O_6$.

The facts from which we draw a conclusion respecting the structure of gynocardin are as follows :

(1) It has the formula $C_{13}H_{19}O_9N$.

(2) It gives a hepta-acetyl derivative.

(3) It is hydrolysed by dilute acids or the enzyme, giving *d*-glucose, hydrogen cyanide, and a third substance.

(4) It is hydrolysed by baryta, giving gynocardinic acid,

$$C_{12}H_{19}O_9{\cdot}CO_2H,$$

and ammonia.

(5) Gynocardinic acid, on treatment with acid, gives *d*-glucose and an acid.

From the foregoing facts, it follows that gynocardin is the *d*-glucose ether of the cyanohydrin of a substance which may be either a trihydroxyaldehyde, $C_5H_4(OH)_3{\cdot}CHO$, or a trihydroxyketone,

$$C_5H_5(OH)_3{:}CO.$$

Since it has been impossible to isolate this substance, and as the quinine salt of its corresponding carboxylic acid was not obtained in an amount sufficient for the further investigation of the latter, its actual constitution could not be determined.

In accordance with the above view, the constitution of gynocardin can be represented by one of the following formulæ:

$$C_5H_4(OH)_3{\cdot}\underset{\displaystyle CN}{\underset{|}{C}H}{\cdot}O{\cdot}C_6H_{11}O_5 \text{ or } C_5H_5(OH)_3{:}\underset{\displaystyle CN}{\underset{|}{C}}{\cdot}O{\cdot}C_6H_{11}O_5.$$

Gynocardinic acid may then be expressed as follows:

$$C_5H_4(OH)_3{\cdot}\underset{\displaystyle CO_2H}{\underset{|}{C}H}{\cdot}O{\cdot}C_6H_{11}O_5 \text{ or } C_5H_5(OH)_3{:}\underset{\displaystyle CO_2H}{\underset{|}{C}}{\cdot}O{\cdot}C_6H_{11}O_5.$$

Experimental.

Estimation of the Hydrogen Cyanide afforded by the Seeds of Gynocardia Odorata (R. Br.).

For this purpose, 25 grams of the seeds were divested of the shells, and the kernels, weighing 17·7 grams, ground to a powder, which was allowed to remain in contact with water (100 c.c.) in a tightly-corked flask for 3 days. The liberated hydrogen cyanide was then driven over by steam, collected in a dilute solution of potassium hydroxide, and estimated by titration with a decinormal solution of silver nitrate, of which 20·5 c.c. were required, whence HCN = 0·63 per cent. in the kernel and 0 44 per cent. in the entire seed.

Isolation of Gynocardin, $C_{13}H_{19}O_9N,1\frac{1}{2}H_2O$.

Four kilograms of the powdered seeds were first extracted with cold petroleum for the complete removal of the fatty oil, and then with 95 per cent. alcohol. On the removal of the alcohol, a dark syrupy residue resulted, which soon formed a paste, consisting chiefly of

a crystalline substance, which was separated from the mother-liquor at the pump. In order to remove the adhering syrupy mother-liquor, the crystalline cake was digested for several minutes with warm ethyl acetate, and again collected by filtration, when it was obtained in a nearly white condition. A further amount of the crude glucoside can readily be obtained from the syrupy alcoholic mother-liquor by first mixing it with prepared sawdust, drying the mass, and then extracting it with ethyl acetate, which slowly removes the glucoside. The whole of the crude glucoside was then dissolved in water, the solution digested with animal charcoal, and the colourless liquid concentrated under diminished pressure to the consistency of a syrup, which, after a short time, formed a hard cake of colourless crystals. This was drained and subsequently dried on porous earthenware. Two hundred grams of the perfectly white, crystalline glucoside were thus obtained. For analysis, the whole was again crystallised from water, and obtained in two successive crops (*a*) and (*b*), consisting of glistening, colourless, prismatic needles. These were dried on porous earthenware in the air. The water of crystallisation was determined by heating the substance at 115° until the weight was constant, and this is not attended by any decomposition of the glucoside. The analyses and determinations of the specific rotatory power were all conducted with the anhydrous substance.

(*a*) 0·7381 lost 0·0560 H_2O. $H_2O = 7·6$.
0·1465 gave 0·2500 CO_2 and 0·0760 H_2O. $C = 46·5$; $H = 5·8$.
0·2071 „ 0·3568 CO_2 „ 0·1058 H_2O. $C = 46·9$; $H = 5·7$.

A solution of 0·5341 in water, made up to 25 c.c., gave, in a 1 dm. tube, $\alpha_D + 1°33'$, whence $[\alpha]_D^{21°} + 72·5°$.

(*b*) 0·6856 lost 0·0464 H_2O. $H_2O = 6·8$.
0·1865 gave 0·3213 CO_2 and 0·0985 H_2O. $C = 47·0$; $H = 5·9$.

A solution of 0·4497 in water, made up to 25 c.c., gave, in a 1 dm. tube, $\alpha_D + 1°18'$, whence $[\alpha]_D + 72·3°$.

The portion (*b*) was again crystallised from water, and the recrystallised substance dried on porous earthenware in the air, and analysed as before.

0·9568 lost 0·0764 H_2O. $H_2O = 8·0$.
0·2279 gave 0·3934 CO_2 and 0·1166 H_2O. $C = 47·1$; $H = 5·7$.
0·6900 „ 24·2 c.c. nitrogen (over KOH sol., sp. gr. 1·3) at 16° and 775 mm. $N = 4·2$.
$C_{13}H_{19}O_9N,1\frac{1}{2}H_2O$ requires $H_2O = 7·5$.
$C_{13}H_{19}O_9N$ requires $C = 46·8$; $H = 5·7$; $N = 4·2$ per cent.

It will be observed that the amount of water initially contained in

(*b*) was less than in (*a*), but that after recrystallisation the percentage of water was increased. The explanation of this is, that when the substance is allowed to separate slowly from a not too concentrated solution it always contains the larger amount of water, but when the conditions are the converse of these, smaller amounts of water are always found.

The molecular weight of gynocardin was very kindly determined for us by Dr. Barger, by his microscopical method (Trans., 1904, **85**, 286).

A solution containing 0·130 gram of anhydrous gynocardin in 1·878 grams of water was found to be isotonic with a solution of cane sugar of the mean concentration of 73·3 grams of the latter in 1000 grams of water:

$$M = \frac{0{\cdot}130 \times 1000}{1{\cdot}878} \times \frac{342}{73{\cdot}3} = 323$$

$C_{13}H_{19}O_9N$ requires M = 333.

It was thus shown that gynocardin crystallises in general with $1\frac{1}{2}$ molecules of water, and that the anhydrous substance has the formula $C_{13}H_{19}O_9N$.

Anhydrous gynocardin melts at 162—163° with slight decomposition; it is very sparingly soluble in all the usual organic solvents except alcohol, in which it readily dissolves on warming, and from which it slowly separates in small needles.

Gynocardin is best crystallised from water, in which it is readily soluble, even in the cold, and from a concentrated solution it separates in glistening, colourless, prismatic needles. It reduces Fehling's solution. No precipitate is formed when either lead acetate or subacetate is added to its aqueous solution. It gives no coloration with ferric chloride or with concentrated sulphuric or nitric acid.

Gynocardin is only slowly hydrolysed by boiling 5 per cent. hydrochloric or sulphuric acid; it is readily attacked by gynocardase, the enzyme contained in the seeds (p. 357), and by emulsin, with generation of hydrogen cyanide, but is not hydrolysed either by diastase or by the animal ferments, ptyalin, pepsin, and pancreatin. In this connection, it may also be stated that gynocardin has been ascertained to be devoid of any appreciable physiological action.

Hepta-acetylgynocardin, $C_{13}H_{12}O_9(C_2H_3O)_7N$.

Gynocardin was dissolved in an excess of hot acetic anhydride, a small amount of anhydrous sodium acetate introduced, and the mixture boiled on a sand-bath during 40 minutes. On shaking with water, the acetyl derivative separated as a white, flocculent precipitate; this was washed, dried on porous earthenware, and recrystallised, first from a

mixture of ethyl acetate and light petroleum, then from a mixture of chloroform and petroleum, and finally from the former mixture of solvents, without any appreciable change in the melting point.

Hepta-acetylgynocardin forms aggregates of fine, white needles melting at 118—119°.

0·1532 gave 0·2907 CO_2 and 0·0736 H_2O. C = 51·8; H = 5·3.
0·1672 „ 0·3180 CO_2 „ 0·0808 H_2O. C = 51·8; H = 5·4.
$C_{13}H_{12}O_9(C_2H_3O)_7N$ requires C = 51·7; H = 5·3 per cent.

A solution of 0·4740 in chloroform, made up to 25 c.c., gave, in a 1 dm. tube, $\alpha_D + 0°46'$, whence $[\alpha]_D + 40·4°$.

Hydrolysis of Gynocardin by Dilute Acids. The Formation of d-*Glucose.*

Gynocardin is only very slowly hydrolysed by heating with 5 per cent. hydrochloric or sulphuric acid, and the reaction is always attended with the formation of a dark secondary product, even when the operation is conducted in an atmosphere of carbon dioxide. In experiments in which two portions of gynocardin of 10 grams each were heated, in the one case for 2 hours on a water-bath with 100 c.c. of 5 per cent. hydrochloric acid, and in the other by boiling for 4 hours with 5 per cent. sulphuric acid, it was possible to recover some unchanged gynocardin, hydrolysis having been far from complete, even with these prolonged periods of heating. The following experiment represents the result of the complete hydrolysis of gynocardin with hydrochloric acid.

Twenty grams of gynocardin were dissolved in 200 c.c. of 5 per cent. hydrochloric acid and the solution heated on a water-bath. Hydrogen cyanide was not present in the liquid until the heating had been in progress for half an hour. After 7 hours' heating, when the solution smelt strongly of hydrogen cyanide and had become brown in colour, steam was passed through it. It then became apparent that hydrolysis had not been complete, for it was necessary to continue the distillation until 2½ litres of liquid had collected before all the hydrogen cyanide was removed. The residual liquid, which contained the non-volatile products of the completely hydrolysed glucoside, was very dark brown, considerable secondary decomposition appearing to have taken place. This solution was neutralised with sodium hydroxide, concentrated considerably under diminished pressure, and extracted with ether, but nothing was removed by the latter. It was therefore mixed with previously extracted sawdust, the mass dried, and extracted with ether, ethyl acetate, and ethyl alcohol respectively. The ether and ethyl acetate extracted nothing, but from the alcoholic extract there

separated a quantity of well-formed crystals; these were collected and recrystallised from water, when they were found to consist of a double compound of *d*-glucose and sodium chloride. By recrystallisation from methyl alcohol, it was possible to remove some of the salt and obtain crystals containing 85 per cent. of the sugar. That this crystalline substance consisted chiefly of *d*-glucose was definitely proved by the formation from it of a phenylglucosazone melting at 206°, and by the determination of its specific rotatory power, when the phenomenon of mutarotation was observed, the value falling to one-half of that first recorded.

A solution of 0·672 in water, made up to 10 c.c., gave, in a 1 dm. tube, $\alpha_D + 5°52'$, and, after the addition of a trace of alkali, $\alpha_D + 2°57'$, whence $[\alpha]_D + 87·3°$ and $+ 43·9°$ respectively.

Action of Barium Hydroxide on Gynocardin. Formation of Gynocardinic Acid, $C_{12}H_{19}O_9·CO_2H$.

Ten grams of gynocardin were dissolved in a hot solution of 20 grams of barium hydroxide in 100 c.c. of water. Ammonia was immediately evolved, and the solution was therefore boiled until the latter was entirely expelled. The excess of barium was then completely removed as carbonate, and the clear, faintly-coloured solution of the barium salt concentrated to a syrupy consistency. By adding alcohol, again evaporating, and repeating this operation several times, the *barium gynocardinate* formed a hard, white, crystalline cake. For analysis, it was heated at 115—120°.

0·5845 gave 0·1605 $BaSO_4$. Ba = 16·2.

$C_{26}H_{38}O_{22}Ba$ requires Ba = 16·4 per cent.

Gynocardinic acid was prepared from the barium salt by exact removal of the barium by sulphuric acid. A strongly acid liquid was thus obtained. This, on concentration under diminished pressure, afforded a nearly colourless syrup, which, even on standing for several days, showed no tendency to crystallise. Gynocardinic acid does not reduce Fehling's solution; its aqueous solution is dextrorotatory.

Action of Dilute Sulphuric Acid on Gynocardinic Acid. Formation of d-*Glucose and an Acid.*

A quantity of gynocardinic acid was heated for several hours on a water-bath with dilute sulphuric acid. The latter was then exactly removed as barium sulphate and the faintly-coloured acid liquid concentrated under diminished pressure. A syrup was thus obtained

which would not crystallise. In addition to the *acid*, it also contained *d*-glucose, for it readily afforded a phenylglucosazone melting at 205°.

In an attempt to separate the acid, the warm aqueous solution of the above syrup was neutralised by the addition of freshly precipitated quinine. The aqueous solution of the quinine salt and glucose, after digesting with animal charcoal, was concentrated considerably under diminished pressure. From the viscous liquid, a small amount of a crystalline salt slowly separated. This was first recrystallised from water, in which it was extremely easily soluble, and then from methyl alcohol, from which it separated in glistening needles, melting at 224° with decomposition. It was dried at 115° and then analysed:

0·1659 gave 0·3884 CO_2 and 0·0988 H_2O. C = 63·8; H = 6·6.
$C_{20}H_{24}O_2N_2,C_7H_{10}O_6$ requires C = 63·0; H = 6·6 per cent.

Although the amount of *quinine salt* thus obtained was too small for further investigation, its isolation is of value, since it affords direct proof that by the hydrolysis of gynocardinic acid a carboxylic acid is formed in addition to *d*-glucose.

Isolation of the Hydrolytic Enzyme, Gynocardase.

One kilogram of the finely-ground seeds was first extracted with cold light petroleum for the removal of the fatty oil, and subsequently digested with water at the ordinary temperature for about 24 hours. To the filtered liquid, about twice its volume of alcohol was added, and, after standing for some hours, the precipitate was collected on a filter, washed with alcohol, and dried in a vacuum over sulphuric acid. When dry, it could be reduced to a light brown powder. The yield corresponded to 2 per cent. of the weight of the seeds.

Gynocardase responds to most of the usual tests for proteid substances. As already stated, it readily hydrolyses gynocardin, and it also hydrolyses amygdalin. It appears, however, to have no action on potassium myronate, in this respect differing from the enzyme contained in *Taraktogenos* seeds (Trans., 1904, **85**, 841).

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XLIII.—*The Action of Ethyl Dibromopropanetetracarboxylate on the Disodium Derivative of Ethyl Propanetetracarboxylate. A Correction.*

By WILLIAM HENRY PERKIN, jun.

A SHORT time ago (Trans., 1903, **83**, 780), T. W. D. Gregory and the author published the results of a research on the action which takes place when the disodium derivative of ethyl propanetetracarboxylate is digested with ethyl dibromopropanetetracarboxylate. It was shown that the decomposition proceeds almost quantitatively with elimination of sodium bromide and formation of a beautifully crystalline ester which melts at 46°.

Some years previously, Perkin and Prentice (Trans., 1891, **59**, 990) had investigated a very similar decomposition, namely, the action which takes place when the disodium derivative of ethyl propanetetracarboxylate is digested with trimethylene bromide. Since the product obtained in this latter case yielded, on hydrolysis and subsequent elimination of carbon dioxide, the *cis*- and *trans*-modifications of hexahydro*iso*phthalic acid, there can be no doubt that it was ethyl hexamethylenetetracarboxylate, the formation of which is readily understood from the equation

$$\begin{array}{l}(CO_2Et)_2CNa\cdot CH_2\cdot CNa(CO_2Et)_2\\ \quad Br\cdot CH_2\cdot CH_2\cdot CH_2Br\end{array} = \begin{array}{c}(CO_2Et)_2C-CH_2-C(CO_2Et)_2\\ CH_2\cdot CH_2\cdot CH_2\end{array} + 2NaBr.$$

Arguing from this experience, as well as from the results which had been obtained in the investigation of many other analogous ring syntheses, Gregory and the author concluded that the decomposition which had taken place when the disodium derivative of ethyl propanetetracarboxylate was digested with ethyl dibromopropanetetracarboxylate was to be represented as follows:

$$\begin{array}{l}(CO_2Et)_2CNa\cdot CH_2\cdot CNa(CO_2Et)_2\\ (CO_2Et)_2CBr\cdot CH_2\cdot CBr(CO_2Et)_2\end{array} = \begin{array}{c}(CO_2Et)_2C\cdot CH_2\cdot C(CO_2Et)_2\\ (CO_2Et)_2C\cdot CH_2\cdot C(CO_2Et)_2\end{array} + 2NaBr,$$

that is to say, the ester melting at 46° was ethyl hexamethyleneoctocarboxylate. On hydrolysis, this ester yielded the corresponding acid (m. p. 220°), which, when heated above its melting point, was decomposed into carbon dioxide and an acid melting at 175°. This

acid was described as *trans*-hexamethylenetetracarboxylic acid, the change just mentioned being represented in the following way :

$$\begin{matrix} (CO_2H)_2C\cdot CH_2\cdot C(CO_2H)_2 \\ (CO_2H)_2C\cdot CH_2\cdot C(CO_2H)_2 \end{matrix} = \begin{matrix} CO_2H\cdot CH\cdot CH_2\cdot CH\cdot CO_2H \\ CO_2H\cdot CH\cdot CH_2\cdot CH\cdot CO_2H \end{matrix} + 4CO_2.$$

Lastly, on treatment with acetic anhydride, the *trans*-acid yielded the anhydride of the corresponding *cis*-acid, which melted at 60°, and was, on hydrolysis, readily converted into the *cis*-acid (m. p. 139—140°).

During the course of a series of experiments similar to those just described, Dr. Max Guthzeit requested Mr. Martin Lobeck * to repeat the above research, with the result that, while able to confirm our experimental work in every detail, he came to the conclusion that the interpretation of the results given by Gregory and the author is certainly incorrect. After carrying out a series of molecular weight determinations, he arrived at the remarkable conclusion that the compounds just mentioned are, without exception, trimethylene derivatives, that is to say, the molecular weights are exactly half those of the hexamethylene derivatives which Gregory and the author assumed had been produced. There is no doubt that Dr. Guthzeit's view is correct, since most of the trimethylene derivatives in question have been obtained by other means, and a careful comparison shows that their properties agree almost exactly with those of the substances obtained by Gregory and the author. The following corrections are therefore necessary in the original paper (Trans., 1903, **83**, 780).

For "ethyl hexamethyleneoctocarboxylate" read "ethyl trimethylenetetracarboxylate."

For "hexamethyleneoctocarboxylic acid" read "trimethylenetetracarboxylic acid."

For "*cis*- and *trans*-hexamethylenetetracarboxylic acids" read "*cis*- and *trans*-trimethylenedicarboxylic acids."

The quantitative formation of a trimethylene derivative by the action of ethyl dibromopropanetetracarboxylate on the disodium derivative of ethyl propanetetracarboxylate is most extraordinary, and, as far as the author knows, entirely without analogy.

When a bromoethereal salt acts on a sodium derivative, the reaction proceeds in such a way that sodium bromide is eliminated and the two residues join together. Thus, for example, when ethyl bromoacetate reacts with the sodium derivative of ethyl malonate, ethyl ethanetricarboxylate is formed :

$$\begin{matrix} CHNa(CO_2Et)_2 \\ CH_2Br\cdot CO_2Et \end{matrix} = \begin{matrix} CH(CO_2Et)_2 \\ CH_2\cdot CO_2Et \end{matrix} + NaBr.$$

But the action which takes place between ethyl dibromopropanetetra-

* The account of these experiments will shortly appear.

carboxylate and the disodium derivative of ethyl propanetetracarboxylate is very different from this. The elimination of sodium bromide leads, apparently, to the formation of two unsaturated molecules which, instead of combining in the usual way to form ethyl hexamethylene-octocarboxylate (p. 358), are each converted into ethyl trimethylene-tetracarboxylate by internal saturation :

$$\begin{matrix}(CO_2Et)_2CNa\cdot CH_2\cdot CNa(CO_2Et)_2 \\ (CO_2Et)_2CBr\cdot CH_2\cdot CBr(CO_2Et)_2\end{matrix} \rightarrow \begin{matrix}(CO_2Et)_2\overset{|}{C}\cdot CH_2\cdot \overset{|}{C}(CO_2Et)_2 \\ (CO_2Et)_2\underset{|}{C}\cdot CH_2\cdot \underset{|}{C}(CO_2Et)_2\end{matrix} \rightarrow$$

$$\begin{matrix} & CH_2 & \\ (CO_2Et)_2C & \triangle & C(CO_2Et)_2 \\ (CO_2Et)_2C & \triangledown & C(CO_2Et)_2 \\ & CH_2 & \end{matrix}.$$

This reaction is another instance of the remarkable ease with which trimethylene derivatives are formed during the course of reactions which might be expected to yield either unsaturated compounds or hexamethylene derivatives.

Many such cases are now known, and the ollowing may be instanced in illustration of this point.

(1) Trimethylene bromide reacts with zinc to form trimethylene,

$$Br\cdot CH_2\cdot CH_2\cdot CH_2Br \rightarrow CH_2<\begin{matrix}CH_2 \\ | \\ CH_2\end{matrix},$$

an l apparently no traces either of propylene (Gustavson, *J. pr. Chem.*, 1899, [ii], **59**, 302) or of hexamethylene are formed during the reaction.

(2) Acetyltı imethylene is produced quantitatively when acetylpropyl bromide is digested with caustic potash (Lipp, *Ber.*, 1889, **22**, 1207 ; Idzowska and E. Wagner, *J. Russ. Phys. Chem. Soc.*, 1898, **30**, 259, 269 ; *Chem. Centr.*, 1898, ii, 474) :

$$CH_3\cdot CO\cdot CH_2\cdot CH_2\cdot CH_2Br \rightarrow CH_3\cdot CO\cdot CH<\begin{matrix}CH_2 \\ | \\ CH_2\end{matrix}.$$

(3) Ethyl α-bromoglutarate is converted by treatment with alcoholic potash or quinoline into trimethylenedicarboxylic acid or its ethyl salt :

$$CO_2Et\cdot CH_2\cdot CH_2\cdot CHBr\cdot CO_2Et \rightarrow CO_2H\cdot CH\overset{CH_2}{\triangle}CH\cdot CO_2H$$

(Bowtell and Perkin, Proc., 1899, **15**, 241 ; see also the following paper by Perkin and Tattersall, p. 362).

Caronic acid is formed in an exactly similar way when ethyl bromodimethylglutarate is digested with alcoholic potash :

$$CO_2Et\cdot CH_2\cdot CMe_2\cdot CHBr\cdot CO_2Et \longrightarrow CO_2H\cdot CH\overset{CMe_2}{\triangle}CH\cdot CO_2H$$

(Perkin and Thorpe, Trans., 1899, **75**, 50).

Preliminary experiments, which have already been made, seem to show that tetra-, penta-, and hexa-methylene rings are not readily formed, if at all, when bromo-compounds similar to those mentioned above are treated with alcoholic potash.

Observations such as these tend to throw doubt on the general applicability of the "Spannungs Theorie" because, according to that theory, four, five, and six membered saturated carbon rings ought to be produced with much greater ease and be much more stable than the three membered carbon ring.

In conclusion, I have to thank Dr. Guthzeit for his kindness in communicating with me privately in regard to this matter and for allowing me to make this correction.

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XLIV.—*Glutaconic Acid and the Conversion of Glutaric Acid into Trimethylenedicarboxylic Acid.*

By WILLIAM HENRY PERKIN, jun., and GEORGE TATTERSALL, B.Sc.

GLUTACONIC ACID has, so far, only been obtained in one modification, although stereochemical theory indicates that the two modifications

$$\begin{matrix} H\cdot C\cdot CH_2\cdot CO_2H \\ \| \\ H\cdot C\cdot CO_2H \\ \textit{cis.} \end{matrix} \quad \text{and} \quad \begin{matrix} H\cdot C\cdot CH_2\cdot CO_2H \\ \| \\ CO_2H\cdot C\cdot H \\ \textit{trans.} \end{matrix},$$

corresponding to maleic and fumaric acids, should exist.

It has been shown by W. H. Perkin, jun., and Alice E. Smith (Trans., 1903, **83**, 8, 771; 1904, **85**, 155) that $\alpha\alpha$-dimethylglutaconic acid, $CO_2H\cdot CMe_2\cdot CH{:}CH\cdot CO_2H$, and $\alpha\alpha\alpha_1$-trimethylglutaconic acid, $CO_2H\cdot CMe_2\cdot CH{:}CMe\cdot CO_2H$, both occur in *cis*- and *trans*-modifications, and this fact makes it all the more remarkable that the parent substance—glutaconic acid itself—is only known in one form.

Glutaconic acid melts at 134°, and when heated with acetyl chloride yields an anhydride which melts at 87° and was first prepared by Buchner (*Ber.*, 1890, **23**, 706). In investigating this anhydride, the authors find that it may be distilled without decomposition under

reduced pressure, and that, as Buchner has stated, it yields, on hydrolysis, the glutaconic acid from which it was prepared. It is therefore certain that the only known modification of glutaconic acid is the *cis*-modification, a view which has already been put forward by Buchner. A large number of experiments were instituted by the authors in the hope of being able to isolate the corresponding *trans*-modification of glutaconic acid, but without success. Several new and interesting facts were, however, brought to light, which may be briefly stated as follows.

When glutaconic acid is distilled, it decomposes into vinylacetic acid and carbon dioxide,

$$CO_2H \cdot CH_2 \cdot CH{:}CH \cdot CO_2H = CO_2H \cdot CH_2 \cdot CH{:}CH_2 + CO_2,$$

but when heated with water in a sealed tube at 180° the decomposition takes place in another direction and crotonic acid results,

$$CO_2H \cdot CH_2 \cdot CH{:}CH \cdot CO_2H = CO_2 + CH_3 \cdot CH{:}CH \cdot CO_2H.$$

Glutaconic acid yields a characteristic anilic acid (m. p. 132°) and is readily acted on by bromine with formation of $\alpha\beta$-dibromoglutaric acid, $CO_2H \cdot CH_2 \cdot CHBr \cdot CHBr \cdot CO_2H$ (m. p. 154—155°).

A series of experiments was next made on the elimination of hydrogen haloids from halogen substitution products of glutaric acid, in the hope that by one, at least, of the methods employed the *trans*-modification of glutaconic acid might be formed.

β-Hydroxyglutaric acid, $CO_2H \cdot CH_2 \cdot CH(OH) \cdot CH_2 \cdot CO_2H$, was prepared by the reduction of acetonedicarboxylic acid (Pechmann and Jenisch, *Ber.*, 1891, **24**, 3250), and then converted into ethyl β-chloroglutarate, $CO_2Et \cdot CH_2 \cdot CHCl \cdot CH_2 \cdot CO_2Et$, by the action of phosphorus pentachloride and then of alcohol. This ester, when treated with diethylaniline and subsequently hydrolysed, yielded *cis*-glutaconic acid. This result is remarkable because, under exactly the same conditions, β-hydroxy-$\alpha\alpha_1$-trimethylglutaric acid,

$$CO_2H \cdot CMe_2 \cdot CH(OH) \cdot CHMe \cdot CO_2H,$$

is converted into *trans*-$\alpha\alpha_1$-trimethylglutaconic acid (Perkin and Smith, Trans., 1903, **83**, 777).

An experiment was also made in which β-hydroxyglutaric acid was subjected to distillation, but the distillate was found to consist of a mixture of *cis*-glutaconic acid and its anhydride.

Ethyl α-bromoglutarate was then prepared from glutaric acid in the usual manner and digested, in one experiment, with alcoholic potash, and in another with diethylaniline, and in both cases the product was found to be *trans*-trimethylenedicarboxylic acid :

$$CH_2{<}\begin{matrix} CHBr \cdot CO_2Et \\ CH_2 \cdot CO_2Et \end{matrix} \longrightarrow CH_2{<}\begin{matrix} CH \cdot CO_2H \\ | \\ CH \cdot CO_2H \end{matrix}.$$

This remarkable formation of a trimethylene derivative had previously

been observed by Bowtell and Perkin (Proc., 1899, **15**, 241), and the experiments described in the present paper entirely confirm the results obtained by these authors.

Lastly, the ethyl α-bromoglutarate just mentioned was converted into ethyl α-iodoglutarate by digesting in alcoholic solution with potassium iodide, and afterwards hydrolysed by means of alcoholic potash, but in this case also the product obtained was *trans*-trimethylenedicarboxylic acid.

The series of experiments just described, together with those carried out by Miss Smith and one of the authors, make it appear probable that the formula usually assigned to glutaconic acid, namely,

$$CO_2H\cdot CH_2\cdot CH\colon CH\cdot CO_2H,$$

does not always correctly represent the constitution of this acid.

The general behaviour of glutaconic acid seems to indicate that its molecule is symmetrical, and the expression

$$CO_2H\cdot \underset{|}{C}H\cdot CH_2\cdot \underset{|}{C}H\cdot CO_2H$$

seems to explain, in a more satisfactory manner, many of the remarkable properties of the acid. Such an expression may be considered as a tautomeric modification of the old formula, and therefore capable of being converted into the latter during the course of certain reactions. The new formula may possibly offer an explanation of the probable existence of only one modification of glutaconic acid, since a substance of this constitution would hardly exist in *cis*- and *trans*-modifications, at all events, of the kind met with in the case of fumaric and maleic acids.

As further evidence in favour of the new formula may be mentioned the fact, recently proved by Dr. J.F. Thorpe, that the positions α and α_1 (α and γ) in glutaconic acid are identical, whereas this could hardly be the case if the acid had the constitution $CO_2H\cdot \overset{\alpha}{C}H_2\cdot CH\colon \overset{\alpha_1}{C}H\cdot CO_2H$. Another interesting observation is the fact that $\alpha\alpha_1$-dimethylglutaconic acid, which according to the new formula would be represented thus:

$$CO_2H\cdot \underset{|}{C}Me\cdot CH_2\cdot \underset{|}{C}Me\cdot CO_2H,$$

exists, like glutaconic acid itself, apparently in one modification only (compare Reformatsky, *Chem. Centr.*, 1898, ii, 886).

As soon, however, as two methyl groups become attached to one α-carbon atom, as in the case of the dimethylglutaconic acid,

$$CO_2H\cdot CMe_2\cdot CH\colon CH\cdot CO_2H,$$

and the trimethylglutaconic acid, $CO_2H\cdot CMe_2\cdot CH\colon CHMe\cdot CO_2H$, the

substances become derivatives of the old formula of glutaconic acid, and at once, just as in the case of fumaric and maleic acids, *cis-trans*-isomerism is observed.

A further discussion of the constitution of glutaconic acid will appear in a paper by Dr. Thorpe, which is shortly to be published.

Experimental.

Glutaconic Acid, its Anhydride and Decomposition Products.

The glutaconic acid employed in these experiments was prepared by the method of Conrad and Guthzeit (*Ber.*, 1882, **15**, 2841), and, after several crystallisations from water, it melted at 134°.

When glutaconic acid is heated in a retort under the ordinary pressure, it melts and gradually darkens in colour; carbon dioxide and water are eliminated, a small quantity of a pungent-smelling acid liquid distils over, and a considerable amount of a carbonaceous mass remains in the retort. The distillate from a number of operations was dissolved in a little ether, dried over calcium chloride, the ether evaporated and the residue twice fractionated, when a mobile liquid was obtained which distilled at about 165° and gave the following results on analysis:

0·1568 gave 0·3196 CO_2 and 0·1022 H_2O. C = 55·6; H = 7·2.
$C_4H_6O_2$ requires C = 55·8; H = 7·0 per cent.

This acid is obviously produced by the elimination of carbon dioxide from glutaconic acid and might therefore be either crotonic acid, *iso*crotonic acid, or vinylacetic acid. When cooled in a freezing mixture, it showed no signs of crystallising, and, since the crotonic acids readily solidify under these conditions, it is probably vinylacetic acid.

When glutaconic acid is distilled under a 12 mm. pressure, an oil passes over between 150—210° and crystallises on cooling. The crystals consist of glutaconic anhydride mixed with a considerable quantity of the unchanged acid.

An experiment was next made on the action of dilute hydrochloric acid on glutaconic acid. The pure acid was dissolved in 5 per cent. hydrochloric acid solution and heated in a sealed tube at 180° for one hour. On opening the tube, a quantity of gas escaped which proved to be carbon dioxide. The liquid was extracted with ether, the ethereal solution dried and evaporated, and the residue distilled, when an oil passed over at 170—180° which, on cooling, partially solidified. The oil was removed by contact with porous porcelain and the residue crystallised from light petroleum, when needle-shaped crystals were obtained which melted at 71—72° and gave the following results on analysis:

0·0838 gave 0·1721 CO_2 and 0·0520 H_2O. C = 56·0; H = 6·8.
$C_4H_6O_2$ requires C = 55·8; H = 7·0 per cent.

The properties of this acid leave no doubt that it was crotonic acid, $CH_3{\cdot}CH{:}CH{\cdot}CO_2H$.

In order to investigate further the properties of glutaconic anhydride, a considerable quantity of this substance was prepared by the method recommended by Buchner (*Ber.*, 1890, **23**, 706), namely, by treating the acid with acetyl chloride. As observed by Buchner, this anhydride, when heated under the ordinary pressure, decomposes at about 130°; but the authors find that, when heated under 15 mm. pressure, it distils for the most part unchanged at 152—153°. The oily distillate solidifies quickly to a mass of needles which, after draining on porous porcelain and recrystallising from ether, melt sharply at 87°.

When the solution of the anhydride (1 gram) in dry ether (150 c.c.) is mixed with aniline (1 gram), a white solid separates, but, on boiling, this again passes into solution. If the bulk of the ether is distilled off and the residue allowed to stand, colourless prisms separate, which, after recrystallisation from ether, melt at 128—132° and consist of *glutaconanilic acid.*

0·2120 gave 12·7 c.c. of nitrogen at 18° and 755 mm. N = 7·2.
$C_{11}H_{11}O_3N$ requires N = 6·9 per cent.

Experiments with Glutaric Acid and its Derivatives.

The first series of experiments was made with β-hydroxyglutaric acid, $CO_2H{\cdot}CH_2{\cdot}CH(OH){\cdot}CH_2{\cdot}CO_2H$, which was prepared in quantity by the reduction of acetonedicarboxylic acid (Pechmann and Jenisch, *Ber.*, 1891, **24**, 3250). It was, however, found unnecessary to carry out the tedious purification by means of the copper salt which these chemists recommend. The product of the reduction is acidified with hydrochloric acid, evaporated to dryness, and extracted with ether in a large Soxhlet apparatus. The ethereal solution, after drying over calcium chloride and evaporating to a small bulk, slowly deposits crystals of pure β-hydroxyglutaric acid. When this hydroxy-acid is distilled under 18 mm. pressure, water is eliminated and the boiling point rises continuously to about 210°. The distillate, which quickly solidifies, consists of a mixture of glutaconic acid and glutaconic anhydride, and not of the acid alone as stated by Pechmann and Jenisch (*loc. cit.*).

Ethyl β-chloroglutarate was prepared from the β-hydroxy-acid in the following way. The hydroxy-acid (6 grams) was left in contact with phosphorus pentachloride (25 grams) in the cold until all action had ceased; the product was then heated for a short time on the water-

bath and poured into 200 c.c. of absolute alcohol. The alcoholic solution was mixed with water, extracted with ether, the ethereal solution washed well with dilute sodium carbonate, dried over calcium chloride, evaporated, and the residue left over sulphuric acid in a vacuum desiccator for two days.

The analysis gave numbers agreeing only approximately with those required.

0·2525 gave 0·1430 AgCl. Cl = 14·0.

$C_9H_{15}O_4Cl$ requires Cl = 16·0 per cent.

The ester thus obtained was heated with about twice its volume of freshly distilled diethylaniline at 150° for 15 minutes; the dark product was poured into dilute hydrochloric acid, extracted with ether, the ethereal solution washed with dilute acid, dried over calcium chloride, and evaporated. The residual oil was hydrolysed with methyl-alcoholic potash and, after removal of the alcohol by the addition of water and evaporation, the residue was acidified and extracted with ether. The solid mass obtained on distilling off the ether was recrystallised from water, when nearly colourless crystals were obtained which melted at 130—132° and consisted of *cis*-glutaconic acid.

The last series of experiments made was with the α-halogen substitution products of glutaric acid. Ethyl α-bromoglutarate,

$$CO_2Et\cdot CHBr\cdot CH_2\cdot CH_2\cdot CO_2Et,$$

was prepared by heating glutaric acid (5 grams) first with phosphorus pentachloride (16 grams) on the water-bath and then with bromine (6·5 grams) in a sealed tube for one hour. The product was poured into excess of alcohol, and, after several hours, water was added and the bromo-ester extracted with ether. The ethereal solution was well washed with dilute sodium carbonate, and evaporated, when ethyl α-bromoglutarate was obtained as an oil which, after standing for some days over sulphuric acid in a vacuum desiccator, was analysed :

0·1803 gave 0·1256 AgBr. Br = 29·4.

$C_9H_{15}O_4Br$ requires Br = 30·0 per cent.

The ethyl α-bromoglutarate thus obtained was mixed with a large excess of a strong solution of methyl-alcoholic potash and heated to boiling for one hour, during which operation a quantity of potassium bromide separated. After adding water and evaporating almost to dryness, the product was acidified with hydrochloric acid and extracted several times with ether. The ethereal solution was dried over calcium chloride and evaporated, when a yellow, oily residue was obtained, which soon deposited a quantity of crystals. The crystals were freed from adhering oil by spreading on porous porcelain, and then crystal-

lised from water, from which the acid separated in prisms melting at 173—174°.

0·1623 gave 0·2755 CO_2 and 0·0672 H_2O. C = 46·3; H = 4·6.
$C_5H_6O_4$ requires C = 46·1; H = 4·6 per cent.

Since this acid was found to be quite stable towards permanganate, it could not be unsaturated, and the only other alternative was that it was a trimethylene derivative. Careful comparison showed that it was *trans*-trimethylenedicarboxylic acid (1, 2), a result which confirms the previous experiments of Bowtell and Perkin (Proc., 1899, **15**, 241). The action of diethylaniline on ethyl α-bromoglutarate was also investigated, and an ester was obtained which, on hydrolysis, again yielded *trans*-trimethylenedicarboxylic acid.

Lastly, ethyl α-iodoglutarate was prepared, and its behaviour on hydrolysis investigated. Ethyl α-bromoglutarate (10 grams) was digested in alcoholic solution with finely powdered potassium iodide (7 grams) for four hours, during which operation much potassium bromide separated. After diluting with water, the product was extracted with ether, the ethereal solution washed with sodium hydrogen sulphite until free from iodine, dried over calcium chloride, and evaporated. After remaining for some hours over sulphuric acid in an exhausted desiccator, the following results were obtained on analysis:

0·1896 gave 0·1349 AgI. I = 38·7.
$C_9H_{15}O_4I$ requires I = 40·4 per cent.

This crude iodo-ester was treated with alcoholic potash in the manner described in the case of the corresponding bromo-ester, with the result that *trans*-trimethylenedicarboxylic acid was again obtained as the principal product of the reaction.

In conclusion, the authors desire to express their thanks to the Research Fund Committee of the Chemical Society for a grant, out of which much of the expense of this research was defrayed.

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XLV.—*Studies in the Camphane Series. Part XVIII. A New Formation of Acetylcamphor.*

By Martin Onslow Forster and Hilda Mary Judd, B.Sc.

Concurrently with experiments on the behaviour of hydroxymethylene camphor towards magnesium alkyl halides, we have studied the course of the Grignard reaction on α-cyanocamphor, and find that whilst about 80 per cent. of the latter escapes attack by magnesium methyl iodide, this agent converts the remainder into the compound

$$C_8H_{14}<\begin{matrix}CH\cdot C(CH_3):NH\\ |\\ CO\end{matrix},$$

which bears to acetylcamphor that relation which the derivative obtained by heating together ammonium formate and benzoylcamphor has to the last-named substance (Forster, Trans., 1903, **83**, 108):

$$C_8H_{14}<\begin{matrix}CH\cdot C(C_6H_5):NH\\ |\\ CO\end{matrix} \qquad C_8H_{14}<\begin{matrix}CH\cdot CO\cdot C_6H_5\\ |\\ CO\end{matrix}.$$

Phenyliminomethylcamphor. Benzoylcamphor.

Dilute hydrochloric acid resolves the new imino-compound quantitatively into ammonia and acetylcamphor, the properties of which are in complete agreement with those described by Brühl (*Ber.*, 1903, **36**, 4282), who first obtained this β-diketone on hydrolysing methyl *C*-acetylcamphorcarboxylate, and more recently by the action of zinc on α-bromocamphor dissolved in ethyl acetate (*Ber.*, 1904, **37**, 755).

The Grignard reaction has been applied to nitriles already by Blaise (*Compt. rend.*, 1901, **132**, 839, 978, and **133**, 1217), who obtained crystalline magnesium compounds of the type $CRR':N\cdot MgI,Et_2O$, yielding ketones when decomposed with water, but the experimental conditions were not favourable to the isolation of an imino-compound. Moreover, the nitriles examined were simple in structure, and in view of the behaviour of other camphor derivatives towards magnesium methyl iodide (Forster, this vol., p. 232), it was considered desirable to ascertain whether the organo-metallic compound attacked the carbonyl group in preference to the cyanogen.

The conversion of α-cyanocamphor into the imine of acetylcamphor led us to expect that the action of magnesium phenyl bromide would give rise to the phenyliminomethylcamphor already mentioned; although there is no difficulty in isolating this compound from the products of reaction, the yield is inferior to that of the acetylcamphor derivative, which is obtainable in quantities comparing favourably with the return from Brühl's process.

The action of magnesium alkyl iodides on hydroxymethylenecamphor is less easy to interpret, owing to the fact that there is produced in each case a mixture of two liquid substances which are separated with difficulty. Moreover, although the chemical investigations of Claisen (*Annalen*, 1894, **281**, 306) and the physical studies of Brühl (*J. pr. Chem.*, 1894, [ii], **50**, 209; *Zeit. physikal. Chem.*, 1900, **34**, 31) have definitely established the enolic constitution of hydroxymethylenecamphor, it is necessary to keep in view the possibility of that substance behaving towards magnesium alkyl halides in the manner associated with aldehydes:

$$C_8H_{14}<\begin{matrix}CH\cdot CHO\\ |\\ CO\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}CH\cdot CHR\cdot OH\\ |\\ CO\end{matrix},$$

the alternative course,

$$C_8H_{14}<\begin{matrix}C:CH\cdot OH\\ |\\ CO\end{matrix} \longrightarrow C_8H_{14}<\begin{matrix}C:CH\cdot OH\\ |\\ CR\cdot OH\end{matrix},$$

being that followed by *iso*nitrosocamphor.

In the case of magnesium methyl iodide, the possible isomeric products would have the empirical formula $C_{12}H_{20}O_2$, but in spite of several modifications in the experiments, the liquid obtained has invariably given results on analysis between those required by this formula and by that of its anhydride. Ultimately an individual substance having the composition $C_{12}H_{18}O$ was isolated by treating with zinc dust in alcohol the crystalline dibromide, $C_{12}H_{18}OBr_2$, produced when the liquid mixture is treated with bromine dissolved in light petroleum. Evidently, therefore, the initial product, $C_{12}H_{20}O_2$, becomes transformed to some extent into its anhydride, which might have the constitution represented by any of the formulæ

$$\text{I. } C_8H_{14}<\begin{matrix}C:CH\cdot CH_3\\ |\\ CO\end{matrix}; \qquad \text{II. } C_8H_{14}<\begin{matrix}C:CH\cdot OH\\ |\\ C:CH_2\end{matrix};$$

$$\text{III. } C_8H_{14}<\begin{matrix}C=\!=\!=CH\\ |\qquad\quad |\\ C(CH_3)\cdot O\end{matrix}.$$

Indifference towards phosphorus pentachloride and the behaviour of the compound towards bromine preclude expression II, whilst the specific rotatory power $[\alpha]_D$ 195° seems inconsistent with that of ethylidenecamphor, Minguin having shown that the latter substance has $[\alpha]_D$ 113°. Moreover, we find that when the α-benzoyl derivative of hydroxymethylenecamphor is treated with magnesium methyl iodide the product is a mixture of the compound $C_{12}H_{18}O$, obtained from hydroxymethylenecamphor itself, with a substance having the empirical formula $C_{19}H_{24}O_3$, from which it doubtless arises by the elimination of benzoic acid; the production of ethylidenecamphor can hardly be

reconciled with this observation, as the α-benzoyl derivative of hydroxymethylenecamphor probably has the constitution

$$C_8H_{14}<\begin{matrix}C:CH\cdot O\cdot CO\cdot C_6H_5\\ | \\ CO\end{matrix}.$$

It is more likely, therefore, that the compound $C_{12}H_{18}O$ belongs to the oxide class and has the constitution represented by formula III, an expression which accords with its indifference towards phosphorus pentachloride, phenylcarbimide, hydroxylamine, and ammoniacal silver oxide, whilst agreeing with the behaviour of the dibromide towards zinc dust, and the readiness with which potassium permanganate oxidises it to camphoric acid.

The action of magnesium ethyl iodide on hydroxymethylenecamphor proceeds on similar lines. In this case, also, a mixture is obtained, consisting, we believe, of the normal compound and the unsaturated oxide derived from it by loss of water :

$$C_8H_{14}<\begin{matrix}C:CH\cdot OH\\ | \\ C(C_2H_5)\cdot OH\end{matrix} \quad \text{and} \quad C_8H_{14}<\begin{matrix}C \equiv\equiv CH\\ | \qquad\quad | \\ C(C_2H_5)\cdot O\end{matrix}.$$

Although fractional distillation fails to separate these two compounds, treatment with bromine gives rise to a crystalline dibromide,

$$C_{13}H_{20}OBr_2,$$

from which the unsaturated oxide, $C_{13}H_{20}O$, may be regenerated by the action of zinc in alcohol. The properties of the substance correspond with those of the lower homologue, $C_{12}H_{18}O$.

Experimental.

Conversion of α-Cyanocamphor into Acetylcamphor and Benzoylcamphor.

Twenty grams of α-cyanocamphor were added to an ice-cold ethereal solution of magnesium methyl iodide prepared from 100 grams of methyl iodide and 14 grams of magnesium powder, the action being very vigorous. On decomposing the product with ice and adding sufficient acetic acid to dissolve the magnesium compounds, a considerable proportion of unchanged cyanocamphor was precipitated, and a further amount was extracted from the ethereal layer by potassium hydroxide. After this treatment, the ether deposited four grams of a crystalline substance on evaporation, and this compound has been identified as the *imine* of acetylcamphor,

$$C_8H_{14}<\begin{matrix}CH\cdot CMe:NH\\ | \\ CO\end{matrix}.$$

The crude material was dissolved in dilute hydrochloric acid, precipitated with potassium hydroxide, dried in the desiccator, and

recrystallised from light petroleum, which deposited striated prisms melting at 126°. A solution containing 0·2659 gram in 25 c.c. of chloroform gave α_D 5°36′ in a 2-dcm. tube, whence $[\alpha]_D$ 263·2°.

0·1099 gave 0·2987 CO_2 and 0·0975 H_2O. C = 74·12; H = 9·86.
$C_{12}H_{19}ON$ requires C = 74·61; H = 9·84 per cent.

The imine obtained in this way decolorises a solution of bromine in chloroform, and when the substance dissolved in dilute sulphuric acid is treated with potassium permanganate, the latter is immediately reduced, a transient yellow coloration, suggesting camphorquinone, being followed by a white, crystalline precipitate, probably consisting of camphoric acid. Hot aqueous alkalis have no effect on the substance, which does not reduce ammoniacal silver oxide or Fehling's solution, but ferric chloride develops an intense blue coloration in alcoholic solutions. Phosphorus pentachloride slowly transforms the compound into an oily product, and benzoyl chloride acts in pyridine without yielding a crystalline derivative. If platinic chloride is added to a solution in alcohol, no change occurs at first, but a precipitate of ammonium platinichloride separates slowly.

The *picrate* separates in minute, yellow needles on mixing warm alcoholic solutions of the imine and picric acid. Recrystallisation resolves a portion of the salt into ammonium picrate, which separates in characteristic, transparent prisms, from which the lustrous needles of the imine salt can be sorted mechanically. The latter substance melts at 143°, forming a deep red liquid which does not evolve gas.

0·1296 gave 15·2 c.c. nitrogen at 22° and 760 mm. N = 13·65.
$C_{12}H_{19}ON,C_6H_3O_7N_3$ requires N = 13·27 per cent.

Hydrolysis to Acetylcamphor and Ammonia.—The substance was dissolved in dilute hydrochloric acid, forming a solution which was clear at first, but gradually became turbid, developing the odour of peppermint. On warming gently, a colourless oil separated, quickly becoming pale yellow; this was collected with ether and dried with calcium chloride, the acid liquid being treated with platinic chloride, which immediately gave an orange-red, crystalline precipitate of ammonium platinichloride. After recrystallisation from boiling water,

0·2849 gave 0·1234 Pt. Pt = 43·31.
$(NH_4)_2PtCl_6$ requires Pt = 43·91 per cent.

On evaporating the dried ethereal extract, a pleasant-smelling oil remained, having all the properties ascribed by Brühl to acetylcamphor (*Ber.*, 1903, **36**, 4282), the odour recalling that of peppermint. It dissolves readily in alkali hydroxides, and in alcoholic

solution develops with ferric chloride an intense bluish-violet coloration, which becomes reddish-violet on dilution with water, and yields a beautiful dark red precipitate with sodium acetate. The characteristic copper derivative described by Brühl was obtained also from our product, and crystallised from petroleum in dark olive-green leaflets melting at 200°.

0·2227 gave 0·0377 CuO. Cu = 13·51.

$(C_{12}H_{17}O_2)_2Cu$ requires Cu = 14·14 per cent.

Formation of Phenyliminomethylcamphor.—Ten grams of α-cyanocamphor were added to a solution of magnesium phenyl bromide prepared from 70 grams of bromobenzene and 9·6 grams of magnesium powder; the ethereal layer obtained on decomposing the magnesium derivative with ice and acetic acid was freed from cyanocamphor by 50 per cent. potassium hydroxide, evaporated in boiling water, and distilled in a current of steam in order to remove bromobenzene and diphenyl. The residue formed a sticky solid, which became granular by treatment with a small quantity of cold alcohol. Dilute hydrochloric acid extracted from this material a substance which crystallised from light petroleum in long, tough, lustrous needles melting at 118°, identical with the compound obtained by heating enolic benzoylcamphor with ammonium formate (Forster, Trans., 1903, **83**, 108).

Action of Magnesium Methyl Iodide on Hydroxymethylenecamphor.

Ten grams of dry, finely powdered hydroxymethylenecamphor were added in small portions to an ice-cold solution of magnesium methyl iodide prepared from 150 c.c. of absolute ether, 50 grams of methyl iodide, and 7 grams of magnesium powder, a somewhat vigorous action taking place. After 12 hours crushed ice was added, followed by 18 grams of acetic acid diluted with water, the bright pink ethereal layer being washed with water and sodium carbonate; on agitation with aqueous potassium hydroxide, the colour disappeared, and a small quantity of unchanged hydroxymethylenecamphor was removed, the ether being then evaporated and the residue distilled in a current of steam. A colourless oil passed over rapidly, having a pleasant, refreshing odour; it was collected with ether, quickly dried with calcium chloride, freed from ether, and distilled, 7 grams boiling at 234° under 765 mm. pressure being obtained.

0·2186 gave 0·6265 CO_2 and 0·1968 H_2O. C = 78·16; H = 10·00.
0·1983 ,, 0·5659 CO_2 ,, 0·1790 H_2O. C = 77·83; H = 10·03.

$C_{12}H_{20}O_2$ requires C = 73·47; H = 10·20 per cent.
$C_{12}H_{18}O$,, C = 80·90; H = 10·11 per cent.

This product had a sp. gr. 0·9639 at 19° and gave α_D 329°20′ in a

2-dcm. tube, whence $[\alpha]_D$ 170·8°; a solution containing 0·4647 gram in 20 c.c. of absolute alcohol at 19° gave α_D 7°40′, whence $[\alpha]_D$ 165·0°. As the analytical results agreed more closely with the composition of the anhydride, $C_{24}H_{38}O_3$, than with either of the formulæ quoted, determinations of molecular weight were made in benzene, giving as a mean result M = 170 ($C_{12}H_{18}O$ requires M = 178; $C_{24}H_{38}O_3$ requires M = 374). The oil decolorised bromine in chloroform and an acidified solution of permanganate immediately in the cold, but gave no coloration with ferric chloride, and although effervescing with phosphorus pentachloride, the action quickly subsided, and appeared disproportionately slight for the amount of material involved.

These observations indicating a mixture, we prepared 60 grams from 100 grams of hydroxymethylenecamphor, and attempted to isolate an individual by fractional distillation, obtaining 30 grams boiling at 229—231° under 757 mm. pressure, the temperature then rising to 240°; the specific rotatory power of this material in alcohol was $[\alpha]_D$ 173·5°, succeeding fractions having $[\alpha]_D$ 170·4° (b. p. 231—232°) and $[\alpha]_D$ 166·3° (b. p. 232—236°). On redistilling the first fraction, the major portion boiled at 229—230°, but the analytical results still lay between those required by the formulæ $C_{12}H_{20}O_2$ and $C_{12}H_{18}O$.

The Dibromide, $C_{12}H_{18}OBr_2$.

Although treatment with alcoholic potassium hydroxide and with concentrated sulphuric acid failed to hydrolyse the anhydride or to dehydrate the hydroxy-derivative, respectively, and so furnish a single substance, it is possible to isolate the anhydride, $C_{12}H_{18}O$, from the foregoing mixture in the form of the dibromide, $C_{12}H_{18}OBr_2$.

The oily product from hydroxymethylenecamphor and magnesium methyl iodide was mixed with chloroform, cooled in ice, and treated with its own weight of bromine in the same solvent. The colour of the halogen was destroyed, and hydrogen bromide, which did not appear at first, was liberated in some quantity as the liquid evaporated; the residue consisted of a yellow oil, in which crystals were embedded, and these were then drained on earthenware and recrystallised twice from boiling light petroleum.

0·2263 gave 0·3491 CO_2 and 0·1105 H_2O. C = 42·07; H = 5·43.
0·3403 „ 0·3803 AgBr. Br = 47·54.
0·2574 „ 0·2866 AgBr. Br = 47·37.
$C_{12}H_{18}OBr_2$ requires C = 42·60; H = 5·32; Br = 47·34 per cent.

The dibromide is readily soluble in cold ether, acetone, chloroform, ethyl acetate, and glacial acetic acid, moderately so in alcohol and light petroleum, crystallising from the last named in long, transparent,

hexagonal prisms, which melt at 152—153° without decomposing. A solution containing 0·2664 gram in 25 c.c. of chloroform gave α_D 3°21′ in a 2-dcm. tube, whence $[\alpha]_D$ 157·2°.

The Compound $C_{12}H_{18}O$, *regenerated from the Dibromide.*

Twenty grams of the dibromide (m. p. 152—153°) were dissolved in 100 c.c. of absolute alcohol sufficiently warm to keep the substance in solution while 20 grams of zinc dust were added slowly; it is necessary to conduct the treatment with zinc very carefully, as the action is liable to proceed beyond control. After half an hour on the water-bath in a reflux apparatus, the alcohol was distilled off and a current of steam passed through the residue without filtering the excess of zinc. The colourless oil was collected with ether, dried with calcium chloride, and distilled, boiling at 227—228° under 764 mm. pressure. Considerable difficulty was experienced in analysing the compound and its homologue, the percentage of carbon being persistently nearly 1 per cent. too low, but the production from, and conversion into, the dibromide, $C_{12}H_{18}OBr_2$, seem to preclude other empirical formulæ.

0·2361 gave 0·6929 CO_2 and 0·2202 H_2O. C = 80·04; H = 10·36.
$C_{12}H_{18}O$ requires C = 80·89; H = 10·11 per cent.

The liquid has a pleasant, camphor-like odour, and is readily volatile in steam. The solution in chloroform decolorises bromine immediately, and on evaporation yields the dibromide from which the substance arises by the action of zinc. The specific rotatory power corresponds more nearly with the lower fractions of the mixture obtained from magnesium methyl iodide and hydroxymethylenecamphor than with the less volatile portion; a solution containing 0·5257 gram in 20 c.c. of chloroform gave α_D 10°15′, whence $[\alpha]_D$ 195·0°.

Oxidation with Potassium Permanganate.—One gram of the oil was shaken with a 2 per cent. solution of potassium permanganate, 100 c.c. of which were required to produce a permanent pink coloration; the filtered liquid was evaporated to small bulk and rendered faintly acid with dilute sulphuric acid. On dissolving the precipitate in sodium carbonate and reprecipitating, camphoric acid was identified; the specimen, when recrystallised from boiling water, did not depress the melting point of the pure substance.

Action of Magnesium Methyl Iodide on the α-Benzoyl Derivative of Hydroxymethylenecamphor.

In their paper on hydroxymethylenecamphor (*Annalen*, 1894, **281**, 314), Bishop, Claisen, and Sinclair describe two isomeric benzoyl

derivatives, the relationship of which has not been explained. Of these, the α-compound (m. p. 119—120°) is obtained by the Schotten-Baumann process of benzoylation, and we have studied the action of magnesium methyl iodide on this compound under the conditions prescribed for hydroxymethylenecamphor itself. The action was less vigorous, and the ultimate product, of which 50 grams were obtained from 90 grams of material, was an oil having an odour of peppermint; this product boiled over a somewhat wide range of temperature, the fraction distilling at 230—235° forming the major portion and giving $[\alpha]_D$ 122·1°.

0·2207 gave 0·6457 CO_2 and 0·1993 H_2O. C = 79·79; H = 10·03.

$C_{19}H_{24}O_3$ requires C = 76·00; H = 8·00 per cent.
$C_{19}H_{22}O_2$ „ C = 80·85; H = 7·80 „
$C_{12}H_{18}O$ „ C = 80·90; H = 10·11 „

The substance, therefore, resembles the compound $C_{12}H_{18}O$, and further decolorises bromine in chloroform and acid potassium permanganate solutions. Its identity with that material was established by converting it into the dibromide, which crystallised from petroleum in lustrous, hexagonal prisms melting at 152°.

0·3183 gave 0·3524 AgBr. Br = 47·12.

$C_{19}H_{22}O_2Br_2$ requires Br = 36·20 per cent.
$C_{12}H_{18}OBr_2$ „ Br = 47·34 „

A solution containing 0·4196 gram in 25 c.c. of chloroform gave α_D 5°15′, whence $[\alpha]_D$ 156·4°. Thus the principal result of treating the α-benzoyl derivative of hydroxymethylenecamphor with magnesium methyl iodide is to produce the oxide, $C_{12}H_{18}O$, identical with that obtained from hydroxymethylenecamphor itself. Nevertheless, a benzoyl compound is present also, because on passing a current of steam through the oil which was drained from the crystalline dibromide, $C_{12}H_{18}OBr_2$, a heavy oil came over having the irritating effect on the eyes produced by benzyl bromide; on heating this liquid with alcoholic potash during several hours and distilling the product in steam, a colourless, heavy, unsaturated oil was obtained, still rich in bromine. Although this compound decolorised bromine in chloroform without losing hydrogen bromide, no crystalline derivative was obtained from it.

Action of Magnesium Ethyl Iodide on Hydroxymethylenecamphor.

Proceeding in the manner described, we obtained from 20 grams of hydroxymethylenecamphor, 14 grams of magnesium, and 100 grams of ethyl iodide dissolved in 400 c.c. of absolute ether, 16 grams of a

pleasant-smelling, colourless oil, the major portion of which distilled at 249—251° under 770 mm. pressure. A solution containing 0·4484 gram in 20 c.c. of chloroform gave α_D 6°46′ in a 2-dcm. tube, whence $[\alpha]_D$ 150·9°.

0·1964 gave 0·5614 CO_2 and 0·1815 H_2O. C = 77·96 ; H = 10·27.
$C_{13}H_{20}O$ requires C = 81·24 ; H = 10·41 per cent.
$C_{13}H_{22}O_2$ „ C = 74·28 ; H = 10·48 „

As in the cases already described, the normal product of action appears to undergo conversion into the anhydride, which we have isolated by the process indicated for the compound $C_{12}H_{18}O$. The oil was mixed with light petroleum and treated with its own weight of bromine in the same medium ; the first portions of the halogen were decolorised, the liquid afterwards remaining red, and yielding on evaporation crystals embedded in oil. The solid product, the weight of which was roughly the same as that of the material employed, after drainage on earthenware was recrystallised first from light petroleum and afterwards from hot alcohol, which deposited long, colourless prisms melting at 88°.

0·2458 gave 0·3925 CO_2 and 0·1255 H_2O. C = 43·55 ; H = 5·67.
0·3347 „ 0·3561 AgBr. Br = 45·27.
$C_{13}H_{20}OBr_2$ requires C = 44·32 ; H = 5·68 ; Br = 45·45 per cent.

The dibromide is moderately soluble in petroleum and in alcohol, dissolving freely in chloroform, benzene, acetone, and glacial acetic acid, crystallising from the last named in long, flat, striated needles on diluting with water. A solution containing 0·5108 gram in 25 c.c. of chloroform gave α_D 5°20′, whence $[\alpha]_D$ 130·5°.

On dissolving the dibromide in warm absolute alcohol and adding zinc dust in small quantities, a very vigorous action took place, and when this had ceased a current of steam was passed through the liquid, the receiver being changed as soon as the alcohol had been removed. A colourless, limpid oil was thus obtained, lighter than water, and having an agreeable, refreshing odour ; it boiled at 236—238° under 745 mm. pressure, and in spite of the difficulty experienced in the combustion of this substance we have no doubt that it is the unsaturated constituent $C_{13}H_{20}O$, forming the major portion of the product from hydroxymethylenecamphor and magnesium ethyl iodide.

0·1240 gave 0·3649 CO_2 and 0·1148 H_2O. C = 80·26 ; H = 10·28.
$C_{13}H_{20}O$ requires C = 81·24 ; H = 10·41 per cent.

A solution containing 0·3834 gram in 20 c.c. of chloroform gave

a_D 6°27′ in a 2-dcm. tube, whence $[a]_D$ 168·2°. Potassium permanganate is immediately reduced by the oil, which decolorises bromine in chloroform, regenerating the dibromide, $C_{13}H_{20}OBr_2$, which melts at 88°.

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XLVI.—*Photographic Radiation of some Mercury Compounds.*

By ROBERT DE JERSEY FLEMING STRUTHERS and JAMES ERNEST MARSH.

WHILE working on the cyanides we lately prepared, by combining mercuric cyanide with phenylhydrazine, a mercury compound having the composition $HgC_2N_2,2(NH_2{\cdot}NH{\cdot}C_6H_5)$, this substance, when freshly obtained, being a colourless, crystalline solid. After studying the compound for a time the idea was impressed on us that it evolved something of the nature of an emanation or radiation. This impression was tested by the following experiments. The film of an "Ilford Ordinary" dry plate was covered by a piece of white paper, and on this a small portion of the substance was laid. The plate thus prepared was allowed to stand in the dark for about ten hours, development being effected by a pyrogallol and sodium carbonate developer. On development, the plate darkened markedly, showing a dark patch underneath the spot where the substance had rested; the compound had therefore acted on the film through the paper. Another slightly different experiment was made. A plate of zinc, perforated with holes, was enclosed between two sheets of paper, and the whole interposed between the photographic plate and the active substance. The exposure lasted thirty-four hours; on development the plate darkened markedly in spots corresponding with the perforations. There was a little darkening observed beneath the zinc, but since Dr. Russell has shown that metallic zinc exerts an action on a photographic plate, this is easily explicable.

These experiments being so far satisfactory, a severer test was applied. Since certain kinds of radiation pass through aluminium, a plate was covered with a sheet of this metal about 0·003 cm. in thickness. On this the substance was placed; no effect, however, was producd, even after many days' exposure. This result is, however, by no means surprising, as Rutherford has shown that 0·0017

cm. of aluminium is sufficient to absorb all the α-rays from radium. When thinner aluminium was employed, quite a different result was obtained. The substance was not placed in contact but exposed at some distance from the plate, which was wrapped in the foil, the film being covered. It was then laid face downwards on a watch-glass containing a small portion of the substance, and to this it was secured by india-rubber bands. After about two days, the plate was removed and developed, when a dark circular patch appeared, coinciding with the area of the watch-glass. It was, however, much denser over the space occupied by the substance. The action was in no way due to the aluminium, for although covered with the foil, no action took place outside the part enclosed by the watch-glass. The exposure lasted about forty hours.

Since quartz is a medium very transparent to certain rays, it was thought desirable to ascertain whether the substance could act through a layer of rock-crystal. A portion of the compound was accordingly placed in a watch-glass, covered by a disc of quartz, and the whole exposed under a dry plate for a couple of days. On the first trial there appeared to be a very slight action; but, on repeating the experiment, no darkening of the film was observable.

Having thus made out a *prima facie* case in favour of some sort of radiation or emanation from the substance, this was likewise tested for any signs of electrical activity. Mr. P. J. Kirkby kindly undertook this for us, but failed to detect any such action.

The photographic action, however, takes place through paper and aluminium foil, both of which, as we have shown, readily stop the massive α-radiation of radium.

We have prepared a copper compound similar in constitution to the active mercuric compound, and have tested it similarly on a plate covered with a perforated sheet of zinc and two pieces of paper. There appeared, however, to be no action—in fact, the space under the perforations seemed in some cases to be clearer than the surrounding film. This effect, again, is readily explicable by Dr. Russell's researches.

To prove whether the mercury compound emits a vapour which might, directly or indirectly, act on a photographic plate, rather more than a gram of substance was kept for several weeks in a desiccator over concentrated sulphuric acid. Any phenylhydrazine vapour, should such be evolved, would at once be absorbed. The substance was weighed at intervals of a day or two. At first there seemed to be practically no loss, but on extending the investigation over a period of some weeks, a small decrease in weight became apparent. After four weeks, the loss had only amounted to 0·14 per cent., equal to five parts per hundred thousand per diem.

The generators of the active mercury compound, namely, mercuric cyanide and phenylhydrazine, were tested separately to ascertain whether they would have, *per se*, any effect on a sensitive film. Phenylhydrazine was found to be active, but the effect was more diffused and sluggish than when in combination. A few drops in a watch-glass placed under a dry plate formed an image, which covered the whole space enclosed by the watch-glass, whereas with our mercury compound the photographic effect was densest immediately above the substance, and much lighter round the edge of the watch-glass. When similarly tested, the other constituent, mercuric cyanide, gave some quite unexpected results. We were prepared to find that this was an inactive substance. However, on exposing a plate over a small quantity contained in a watch-glass for about twenty-four hours, it produced a fairly strong image, which coincided with the outline of the substance, and did not extend to the edge of the watch-glass. It had a striated appearance, and seemed such as might have been caused by a sort of bombardment of particles from the substance rather than by a slowly diffusing vapour. We therefore determined to investigate the action of this substance more fully. Some of the cyanide was placed in a tube, and heated by the flame of a bunsen burner. After the usual decrepitation had ceased and the substance was on the verge of decomposition, it was allowed to cool. The cyanide thus prepared was exposed under a photographic plate as before. On development, no trace of action was visible. The heating had rendered the mercuric cyanide inert.

Having devised a method by which mercuric cyanide might be distilled in a high vacuum without any decomposition such as occurs when it is heated under ordinary atmospheric pressure, some of the substance was placed in a small retort and volatilised by this method. The tube of the retort in which the distillate had condensed was cut into cross sections, and the contents of each exposed separately under a photographic plate to find whether the active principle had again condensed at any part of the tube. None of these sections, however, proved to be active.

Mercuric cyanide, therefore, is not active under all conditions. We desired to find out whether this activity is general or acquired, or whether it is owing to an impurity contained in the salt? To throw some light on this subject we tested as many specimens of the cyanide as were to be found in our laboratories. Of several samples, all were found active but one, and this was apparently a very old specimen. A specimen of the salt prepared from inactive mercuric oxide and carefully prepared hydrocyanic acid was found to be active. When mercuric cyanide was covered by a layer of

water and the whole exposed under a plate, there was no action. When, however, inactive mercuric cyanide was slightly moistened with water, it became active.

After having discovered that mercuric chloride is very active, which we did early in the investigation, we thought it highly probable that the somewhat weaker activity of the cyanide might be due to the presence of traces of the chloride. This idea was strengthened by the fact that mere traces of mercuric chloride, when added to inactive cyanide, produced an active mixture. The most careful investigation, however, failed to reveal the slightest contamination with mercuric chloride in some of the most active specimens of mercuric cyanide. The active effect is, therefore, apparently quite independent of the presence of chloride, and as it still appeared in the mercuric cyanide, which was prepared by us with the greatest care from pure materials, as above stated, this idea may be dismissed as most improbable.

The tests to which we subjected mercuric chloride showed this substance to be very active. A plate exposed over a small quantity in a watch-glass darkened strongly on development. In order to test whether this resembled the cyanide in its behaviour after heating, a few grams were distilled under ordinary atmospheric pressure until about two-thirds had passed over into the receiver. Small portions of distillate and residue were each exposed in a separate receptacle under the same dry plate. On developing the plate, both portions produced images of about equal intensity. The distillate formed rather a larger and wider image, but this difference may have been merely accidental. The chloride, therefore, is unlike the cyanide, since its activity persists unchanged after heating and distilling.

Mercuric cyanide and chloride having proved to be active, it seemed possible that other compounds of the metal might produce similar effects. Accordingly, mercuric bromide, iodide, nitrate, sulphate, acetate, sulphide, oxide, and mercuric ammonium chloride were tested, as were also mercurous chloride, nitrate, sulphate, acetate, and oxide. Of these, the bromide and both the nitrates were active, but all the other salts were inactive or at most very slightly active.

Redistilled metallic mercury was found to be quite inactive as regards an ordinary dry plate.

Silver cyanide, either white or when darkened by light, had no action; neither was cuprous cyanide active.

XLVII.—*Nitrogen Halogen Derivatives of the Aliphatic Diamines.*

By Frederick Daniel Chattaway.

Although a few substances obtained by the direct action of the halogens on simple aliphatic primary amines were among the earliest nitrogen chlorides and bromides to be prepared, and although the quinonedichloroimides derived from aromatic diamines have long been known and have recently received important industrial applications, no compounds of this nature have hitherto been obtained from the aliphatic diamines.

The aliphatic diamines themselves, however, and the diacyldiamines readily yield compounds in which the whole of the hydrogen attached to nitrogen is replaced by halogen, and in the course of a systematic investigation of compounds of this type on which the author is engaged, a number of derivatives of ethylenediamine and trimethylenediamine have been prepared. The most noteworthy compounds obtained are those yielded by ethylenediamine itself, ethylenetetrachlorodiamine, $NCl_2{\cdot}CH_2{\cdot}CH_2{\cdot}NCl_2$, and ethylenetetrabromodiamine, $NBr_2{\cdot}CH_2{\cdot}CH_2{\cdot}NBr_2$, which approach the simple halogen derivatives of nitrogen more nearly in composition than any compounds yet known or which are likely to be prepared. Both are stable substances; the former is a limpid, yellow liquid resembling nitrogen chloride in colour, pungent odour, and explosibility, the latter a beautifully crystalline, orange-red solid which is also extremely explosive.

Ethylenetetrachloroaminodiamine, $NCl_2{\cdot}CH_2{\cdot}CH_2{\cdot}NCl_2$.

This compound was prepared by dissolving ethylenediamine (1 mol.) in 50 per cent. acetic acid (6 mols.) and adding this liquid slowly to a large excess of a cooled saturated solution of bleaching powder. The tetrachloroamine then separated as a pale yellow liquid and was extracted by chloroform; on separating the chloroform solution, drying it with fused calcium chloride, and evaporating off the solvent in a current of air, it was obtained anhydrous and in a pure state.

Ethylenetetrachlorodiamine is a limpid, bright yellow liquid, which does not solidify when cooled in a mixture of ice and salt; it decomposes, sometimes with explosion, when heated under the ordinary atmospheric pressure, but can be distilled unchanged under diminished pressure; it boils at 116° under 50 mm. pressure. When a small quantity contained in a capillary tube is placed directly in a flame, it explodes with great violence. It is comparatively stable at the ordinary

temperature, not undergoing any appreciable decomposition when kept for some weeks in a dry atmosphere.

It gives off a very pungent and irritating vapour, which violently attacks the eyes and has a peculiar smell very characteristic of the chloroamines and recalling that of nitrogen chloride itself.

This compound and all others described in the paper were analysed by dissolving them in acetic acid, adding to the solution potassium iodide, and titrating the iodine thus liberated with standard sodium thiosulphate.

0·1767 liberated I = 71·5 c.c. *N*/10 I. Cl (as NCl) = 71·72.
$C_2H_4N_2Cl_4$ requires Cl (as NCl) = 71·65 per cent.

Ethylenetetrabromodiamine, $NBr_2\cdot CH_2\cdot CH_2\cdot NBr_2$.

A solution of ethylenediamine in the equivalent quantity of acetic acid was poured into a considerable excess of a cooled decinormal solution of hypobromous acid, when a pale yellow solid at once separated. Chloroform was then added and the whole shaken for some time, but the solid only partially dissolved. The undissolved portion was filtered off and dried over phosphoric oxide in a vacuum. It slowly evolved bromine at the ordinary temperature, and could not be recrystallised from any solvent without decomposition; it appears to be a bromine additive product of a partially substituted ethylenediamine. As its composition varied with the manner of drying and the length of time it was kept, it was not further investigated.

The filtered chloroform solution, on drying and evaporating off the solvent, deposited the ethylenetetrabromoamine as a beautifully crystalline, orange-coloured solid. When crystallised from chloroform, in which it is easily soluble, it separated in brilliant, orange-red, short, six-sided, flattened prisms with domed ends.

0·4084 liberated I = 86·8 c.c. *N*/10 I. Br (as NBr) = 84·97.
$C_2H_4N_2Br_4$ requires Br (as NBr) = 85·07 per cent.

It melts at 62°, and if heated a few degrees higher gives off gas, and almost at once explodes with a very violent detonation. It remains unchanged for some days in a dry atmosphere, but if kept for several weeks slowly decomposes giving off bromine and leaving behind a black, tarry mass.

s-*Diacetylethylenedichlorodiamine,*
$CH_3\cdot CO\cdot NCl\cdot CH_2\cdot CH_2\cdot NCl\cdot CO\cdot CH_3$.

s-Diacetylethylenediamine was dissolved in water and mixed with an excess of a solution of hypochlorous acid made by dissolving potass-

ium hydrogen carbonate in a solution of sodium hypochlorite. The dichloroamine produced, being soluble in water, remained dissolved, and was extracted by shaking the solution several times with chloroform. After separating and drying the chloroform solution with calcium chloride, the solvent was driven off in a current of air, when the dichloroamine was left as a white, crystalline mass; it is moderately soluble in chloroform, very sparingly so in petroleum. It was dissolved in chloroform, and a little warm petroleum added, when it crystallised in short, colourless, transparent prisms terminated by pyramids (m. p. 94°).

0·2190 liberated I = 41 c.c. *N*/10 I. Cl as NCl = 33·18.
$C_6H_{10}O_2N_2Cl_2$ requires Cl as NCl = 33·27 per cent.

It is a comparatively stable substance, but decomposes slightly, giving off chlorine, when kept for some months, even in a dry atmosphere and when the light is excluded.

s-*Diacetylethylenedibromodiamine*,
$CH_3·CO·NBr·CH_2·CH_2·NBr·CO·CH_3$.

This compound was prepared and crystallised exactly as the corresponding dichloroamine, using, however, a decinormal solution of hypobromous acid made by shaking precipitated mercuric oxide suspended in water with bromine; it crystallises in short, transparent, very pale yellow prisms. On heating, it reddens and melts at about 150—155°, giving off bubbles of gas, and almost immediately explodes.

0·2418 liberated I = 31·9 c.c. *N*/10 I. Br as NBr = 52·74.
$C_6H_{10}O_2N_2Br_2$ requires Br as NBr = 52·94 per cent.

s-*Dipropionylethylenediamine*, $C_2H_4(NH·CO·C_2H_5)_2$.

This and a number of other diacyl derivatives of the aliphatic diamines not previously described were prepared by adding the diamine cautiously to the calculated quantity of the corresponding acid anhydride or chloride dissolved in ether. After the first vigorous action, which was always accompanied by the separation of the diacyl derivative, was over the product was warmed on the water-bath to drive off the ether and the residue heated for a short time with an aqueous solution of the calculated quantity of potassium hydrogen carbonate. The product was then recrystallised from a suitable solvent, chloroform, alcohol, or glacial acetic acid being used according to the solubility of the compound.

s-Dipropionylethylenediamine crystallises from alcohol, in which it is easily soluble, in small, colourless plates (m. p. 192°).

s-*Dipropionylethylenedichlorodiamine*,
$CH_3 \cdot CH_2 \cdot CO \cdot NCl \cdot CH_2 \cdot CH_2 \cdot NCl \cdot CO \cdot CH_2 \cdot CH_3$.

This compound was prepared by shaking a solution of *s*-dipropionylethylenediamine in chloroform with excess of a solution of hypochlorous acid and treating as before; it was obtained as a pale yellow, limpid, highly refractive liquid with a smell resembling hypochlorous acid; it showed no sign of crystallisation, even after standing in a vacuum over phosphoric oxide for several weeks. When strongly heated, it decomposes almost explosively.

0·3244 liberated I = 53·7 c.c *N*/10 I. Cl as NCl = 29·34.
$C_8H_{14}O_2N_2Cl_2$ requires Cl as NCl = 29·41 per cent.

s-*Dipropionylethylenedibromodiamine*,
$CH_3 \cdot CH_2 \cdot CO \cdot NBr \cdot CH_2 \cdot CH_2 \cdot NBr \cdot CO \cdot CH_2 \cdot CH_3$.

This compound, prepared as previously described, crystallises in transparent, slender, flattened, pale yellow prisms; it melts at 112° and when more strongly heated decomposes explosively at about 160°.

0·2306 liberated I = 27·9 c.c. *N*/10 I. Br as NBr = 48·37.
$C_8H_{14}O_2N_2Br_2$ requires Br as NBr = 48·44 per cent.

s-*Diphenylacetylethylenediamine*, $C_2H_4(NH \cdot CO \cdot CH_2 \cdot C_6H_5)_2$, crystallises from alcohol, in which it is moderately soluble, in large, thin, glittering, six-sided, colourless plates (m. p. 207°).

s-*Diphenylacetylethylenedichlorodiamine*,
$C_6H_5 \cdot CH_2 \cdot CO \cdot NCl \cdot CH_2 \cdot CH_2 \cdot NCl \cdot CO \cdot CH_2 \cdot C_6H_5$,
prepared as previously described, is obtained as a viscid, oily, pale yellow liquid which very slowly solidifies; it crystallises from a mixture of chloroform and light petroleum in small, colourless, four-sided plates which melt at 65°.

0·3978 liberated I = 43·1 c.c. *N*/10 I. Cl as NCl = 19·2.
$C_{18}H_{18}O_2N_2Cl_2$ requires Cl as NCl = 19·42 per cent.

s-*Diphenylacetylethylenedibromodiamine*,
$C_6H_5 \cdot CH_2 \cdot CO \cdot NBr \cdot CH_2 \cdot CH_2 \cdot NBr \cdot CO \cdot CH_2 \cdot C_6H_5$,
crystallises from a mixture of chloroform and petroleum in clusters of transparent, very pale yellow plates; it melts at 128°, and if heated rapidly above this temperature explodes at about 150°.

0·2272 liberated I = 19·8 c.c. *N*/10 I. Br as NBr = 34·84.
$C_{18}H_{18}O_2N_2Br_2$ requires Br as NBr = 35·21 per cent.

s-*Dibenzoylethylenedichlorodiamine*,
$C_6H_5 \cdot CO \cdot NCl \cdot CH_2 \cdot CH_2 \cdot NCl \cdot CO \cdot C_6H_5$.

This compound was prepared by slowly adding an excess of a solution of bleaching powder to a well-cooled solution of *s*-dibenzoylethylenediamine in glacial acetic acid. The dichloroamine, which separated at first as a yellow, viscid liquid, was extracted with chloroform, and this solution shaken with a fresh solution of hypochlorous acid made from potassium hydrogen carbonate and sodium hypochlorite. On separating and drying the solution, and driving off the chloroform in a current of air, the dichloroamine was left as a beautifully crystalline solid. It crystallises from chloroform, in which it is sparingly soluble, in glittering, transparent, colourless, four-sided, rhombic plates, which are apparently flattened rhombs. It melts at 162°, and when heated a few degrees higher decomposes, giving off bubbles of gas.

0·3160 liberated I = 37·7 c.c. *N*/10 I. Cl as NCl = 21·14.
$C_{16}H_{14}O_2N_2Cl_2$ requires Cl as NCl = 21·03 per cent.

s-*Dibenzoylethylenedibromodiamine*,
$C_6H_5 \cdot CO \cdot NBr \cdot CH_2 \cdot CH_2 \cdot NBr \cdot CO \cdot C_6H_5$.

This compound was prepared by adding a solution of *s*-dibenzoylethylenediamine in glacial acetic acid to a well-cooled solution of hypobromous acid. The solid which separated was dissolved in glacial acetic acid and the solution again added to well-cooled hypobromous acid solution. The dibromoamine was then dried and recrystallised from chloroform, in which it is sparingly soluble; it crystallises in small, brilliant, transparent, four-sided, very pale yellow plates. When quickly heated at about 180—182°, it melts with reddening and decomposition, but the melting point varies with the time taken in heating, as decomposition begins before the compound melts.

0·3032 liberated I = 28·4 c.c. *N*/10 I. Br as NBr = 37·45.
$C_{16}H_{14}O_2N_2Br_2$ requires Br as NBr = 37·53 per cent.

s-*Di*-m-*nitrobenzoylethylenediamine*, $C_2H_4(NH \cdot CO \cdot C_6H_4 \cdot NO_2)_2$, crystallises from glacial acetic acid, in which it is very sparingly soluble, in small, colourless needles with a faint yellow tint (m. p. 257°).

s-*Di*-m-*nitrobenzoylethylenedichlorodiamine*,
$C_6H_4(NO_2) \cdot CO \cdot NCl \cdot CH_2 \cdot CH_2 \cdot NCl \cdot CO \cdot C_6H_4(NO_2)$ [benzene rings drawn with NO_2 substituents].

This and the other dichloroamines derived from diacyl compounds only sparingly soluble in glacial acetic acid were prepared by rapidly

adding bleaching-powder solution to a warm solution of the amide in glacial acetic acid. It crystallises from chloroform, in which it is very sparingly soluble, in brilliant, small, transparent, colourless plates with a slight yellow tint. It melts at 173°, and on further treating remains apparently unchanged up to 220°, but when heated rapidly in a flame decomposes explosively.

0·2236 liberated I = 20·8 c.c. *N*/10 I. Cl as NCl = 16·49.
$C_{16}H_{12}O_6N_4Cl_2$ requires Cl as NCl = 16·6 per cent.

s-*Di*-p-*nitrobenzoylethylenediamine*, $C_2H_4(NH{\cdot}CO{\cdot}C_6H_4{\cdot}NO_2)_2$, crystallises from glacial acetic acid, in which it is sparingly soluble, in pale yellow, irregularly grown prisms (m. p. 254°).

s-*Di*-p-*nitrobenzoylethylenedichlorodiamine*,
$NO_2\langle C_6H_4\rangle CO{\cdot}NCl{\cdot}CH_2{\cdot}CH_2{\cdot}NCl{\cdot}CO\langle C_6H_4\rangle NO_2$,

is very sparingly soluble in chloroform, from which it crystallises in small, colourless plates with a faint yellow tint (m. p. 207°). When heated more strongly, it decomposes with evolution of gas at about 215°, and explodes when rapidly heated in a flame.

0·1325 liberated I = 12·4 c.c. *N*/10 I. Cl as NCl = 16·59.
$C_{16}H_{12}O_6N_4Cl_2$ requires Cl as NCl = 16·6 per cent.

s-*Dibenzenesulphonylethylenedichlorodiamine*,
$C_6H_5{\cdot}SO_2{\cdot}NCl{\cdot}CH_2{\cdot}CH_2{\cdot}NCl{\cdot}SO_2{\cdot}C_6H_5$.

This compound was prepared by adding bleaching-powder solution to a solution of the amide in glacial acetic acid, extracting with chloroform, and treating as before described; it crystallises from a mixture of chloroform and light petroleum in clusters of slender, colourless prisms. It melts at 113° and can be heated to 200° with very slight decomposition; when heated strongly in a flame, it decomposes explosively.

0·2787 liberated I = 27·2 c.c. *N*/10 I. Cl as NCl = 17·3.
$C_{14}H_{14}O_4N_2Cl_2S_2$ requires Cl as NCl = 17·32 per cent.

s-*Dibenzenesulphonylethylenedibromodiamine*,
$C_6H_5{\cdot}SO_2{\cdot}NBr{\cdot}CH_2{\cdot}CH_2{\cdot}NBr{\cdot}SO_2{\cdot}C_6H_5$,

crystallises from a mixture of chloroform and light petroleum in clusters of pale yellow prisms (m. p. 134°). On heating above this temperature, it decomposes, reddening and evolving gas at about 160—175°. When heated rapidly in a flame, it explodes.

0·3667 liberated I = 29·4 c.c. *N*/10 I. Br as NBr = 32·05.
$C_{14}H_{14}O_4N_2Br_2S_2$ requires Br as NBr = 32·1 per cent.

Di-p-*toluenesulphonylethylenedichlorodiamine*,

$$CH_3\langle C_6H_4 \rangle SO_2{\cdot}NCl{\cdot}CH_2{\cdot}CH_2{\cdot}NCl{\cdot}SO_2\langle C_6H_4 \rangle CH_3.$$

This compound is moderately easily soluble in chloroform, and crystallises in long, colourless, very slender prisms. It melts at 136° and can be heated to 200° with no apparent change, but at 200—210° it decomposes rapidly with evolution of gas.

0·3524 liberated I = 32·3 c.c. *N*/10 I. Cl as NCl = 16·24.
$C_{16}H_{18}O_4N_2Cl_2S_2$ requires Cl as NCl = 16·21 per cent.

Di-p-*toluenesulphonylethylenedibromodiamine*,

$$CH_3\langle C_6H_4 \rangle SO_2{\cdot}NBr{\cdot}CH_2{\cdot}CH_2{\cdot}NBr{\cdot}SO_2\langle C_6H_4 \rangle CH_3.$$

This compound crystallises extremely well in clusters of pale yellow, transparent, glittering plates; it melts at 165°, and, on heating to about 170°, it reddens and begins rapidly to decompose, evolving bubbles of gas; if heated rapidly at about 180°, it explodes.

0·3087 liberated I = 23·4 c.c. *N*/10 I. Br as NBr = 30·31.
$C_{16}H_{18}O_4N_2Br_2S_2$ requires Br as NBr = 30·39 per cent.

Di-m-*nitrobenzenesulphonylethylenediamine*,

$$C_2H_4(NH{\cdot}SO_2{\cdot}C_6H_4{\cdot}NO_2)_2,$$

crystallises from glacial acetic acid in very small, colourless plates with a faint yellow tint and melts somewhat indefinitely at 189—191°.

Di-m-*nitrobenzenesulphonylethylenedichlorodiamine*,

$$(NO_2)C_6H_4\rangle SO_2{\cdot}NCl{\cdot}CH_2{\cdot}CH_2{\cdot}NCl{\cdot}SO_2\langle C_6H_4(NO_2).$$

This compound, which was prepared by adding bleaching-powder solution in excess to a hot solution of the amide in glacial acetic acid, is so sparingly soluble in chloroform that it was recrystallised from glacial acetic acid, in which it is moderately soluble; it crystallises in very small, short, pale yellow prisms (m. p. 198°). When heated to 220°, it apparently undergoes little decomposition, the melted substance only slightly reddening; it explodes, however, when heated in a flame.

0·2820 liberated I = 22·4 c.c. *N*/10 I. Cl as NCl = 14·08.
$C_{14}H_{12}O_8N_4Cl_2S_2$ requires Cl as NCl = 14·26 per cent.

Dibenzoyltrimethylenedichlorodiamine,
$C_6H_5 \cdot CO \cdot NCl \cdot CH_2 \cdot CH_2 \cdot CH_2 \cdot NCl \cdot CO \cdot C_6H_5$.

The trimethylene-dichlorodiamines and -dibromodiamines are prepared as easily as those derived from ethylenediamine and by similar methods. Dibenzoyltrimethylenedichlorodiamine is easily soluble in chloroform, and crystallises from a mixture of this with light petroleum in brilliant, colourless plates; it melts at 84° and decomposes violently when rapidly heated to about 160°.

0·3005 liberated I = 34·3 c.c. $N/10$ I. Cl as NCl = 20·23.
$C_{17}H_{16}O_2N_2Cl_2$ requires Cl as NCl = 20·19 per cent.

Dibenzenesulphonyltrimethylenediamine, $C_3H_6(NH \cdot SO_2 \cdot C_6H_5)_2$.

This compound crystallises from alcohol, in which it is very easily soluble, in long, colourless plates (m. p. 96°).

Dibenzenesulphonyltrimethylenedichlorodiamine,
$C_3H_6(NCl \cdot SO_2 \cdot C_6H_5)_2$.

This compound is easily soluble in chloroform; it crystallises from this solvent mixed with light petroleum in small, transparent, colourless plates (m. p. 134°).

0·2668 liberated I = 25·3 c.c. $N/10$ I. Cl as NCl = 16·81.
$C_{15}H_{16}O_4N_2Cl_2S_2$ requires Cl as NCl = 16·75 per cent.

Other diamines, for example, pentamethylenediamine, and their acyl derivatives yield similarly chloroamino- and bromoamino-derivatives. These resemble in general properties the compounds previously described, but have not been yet obtained in a well-crystallised form, probably on account of the diamines used not being perfectly pure, for it has been noted with all other classes of substituted nitrogen chlorides and bromides that the difficulty of obtaining a crystalline product is very greatly increased by quite an insignificant amount of impurity.

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XLVIII.—*Transformations of Highly Substituted Nitro-aminobenzenes.*

By Kennedy Joseph Previté Orton and Alice Emily Smith.

A characteristic property of the nitroamines of the aromatic series —the nitroamines derived from the anilines—is their ready change into the isomeric nitroanilines, the nitro-group wandering from the amino-group to one of the carbon atoms in the nucleus. In this change, the nitro-group always becomes attached to a carbon atom which is either ortho- or para- with respect to the amino-group, and never to the carbon atoms, which are in the meta-position relative to this group (Bamberger and others, *Ber.*, 1893, **26**, 471, 485; 1894, **27**, 584; 1895, **28**, 401). The 2 : 4 : 6-trisubstituted nitroamino-benzenes, in which both the ortho- and para-positions relative to the amino-group are occupied by atoms or groups other than hydrogen, have as yet been little studied; they were first obtained by one of us (Trans., 1902, **81**, 490) by the carefully regulated action of nitric acid on *s*-trisubstituted anilines dissolved in acetic acid. 1-Nitroamino-2 : 4 : 6-trichloro- and 1-nitroamino-2 : 4 : 6-tribromo-benzenes were thus prepared. Later (Trans., 1902, **81**, 806), it was found that these and analogously constituted anilines could be practically quantitatively converted into nitroamines by treatment of their solutions in acetic acid with nitric acid and acetic anhydride.

Since the ortho- and para-positions are occupied in these nitroamines, it is no longer possible for these compounds to change into isomeric nitroanilines. It was found, however, that a transformation did take place, the products varying according to the nature of the groups or atoms attached to the carbon atoms in these positions. Thus, when bromine was in the para-position relative to the nitroamino-group, it was displaced by the nitro-group, a substituted *p*-nitroaniline being formed, thus:

$NH{\cdot}NO_2$ (Br, Br, Br ring) $\longrightarrow$ NH_2 (Br, Br, NO_2 ring).

Although chlorine is also similarly capable of being replaced by the nitro-group, such a change does not occur under the same conditions of temperature, &c., as in the case of bromine.

The transformation of the nitroaminobenzenes into nitroanilines

only occurs in acid solution * and may be in many cases easily brought about by keeping for several hours a solution of the nitroamine in acetic acid to which a few drops of concentrated sulphuric acid have been added. If a higher concentration of sulphuric acid is used, the change can be effected in a few minutes.

When solutions of nitroamines in glacial acetic acid are treated with sulphuric acid, a characteristic indigo, magenta, or purple coloration is developed. This coloration is observed with nitroamines of very varying constitution, both with *s*-trisubstituted and with less highly substituted nitroaminobenzenes. The products, however, obtained on diluting these solutions with ice are very different in the two cases. If one of the ortho-positions or the para-position is unoccupied, as in 2 : 4-dichloronitroaminobenzene or in 2 : 6-dibromonitroaminobenzene, a yellow precipitate of the isomeric nitroanilines is formed on dilution. But if the ortho- and the para-positions are occupied, a red solid is obtained which may contain a substituted *p*-nitroaniline in the case of anilines in which the para-position relative to the nitroamino-group is occupied by bromine, for example, *s*-tribromoaniline; in the case of such a nitroamine as that derived from *s*-trichloroaniline, no nitroaniline is present.

It is the object of this investigation to throw light on the nature of these red solids, and, if possible, on the mechanism of the reaction in which they and the nitroanilines are formed. Since the decomposition of 1-nitroamino-*s*-trichlorobenzene is not complicated by the replacement of the *p*-chlorine atom by the nitro-group, this substance has been chosen for a detailed study.

With proper precautions, the treatment of the nitroamino-*s*-trichlorobenzene leads to the formation of the red solid, *s*-trichlorobenzenediazonium salts, and ammonia. No chlorine is eliminated in the reaction if the temperature is not allowed to rise above 15°. The red solid has been found to be s-*trichlorophenyliminotrichlorobenzoquinone* (hexachloroquinoneanil),

Cl Cl Cl
Cl⟨ ⟩N:⟨ ⟩:O,
Cl Cl

since when heated with sulphuric acid it is decomposed quantitatively into *s*-trichloroaniline and trichloroquinone.

It will be noted that in the formation of this compound from the nitroamine, in which the three chlorine atoms are symmetrically placed,

* In alkaline solution, the nitroamines are present as salts, which are probably derivatives of an iminonitronic acid, R·N:NO·OH. When set free from its salts, this acid changes into the isomeric nitroamine, the ψ-acid.

one of the chlorine atoms has changed its point of attachment to a neighbouring carbon atom.

The iminoquinone can be reduced to the corresponding *hexachloro-hydroxydiphenylamine*,

Cl Cl Cl
Cl⟨ ⟩NH⟨ ⟩·OH,
Cl Cl

which in benzene solution can be again oxidised to the iminoquinone by mercuric oxide.

The phenyliminoquinone, which represents about 30 per cent. of the nitroamine, and the ammonia are formed in molecular proportions, the remainder of the nitroamine being converted into diazonium salt.

The hexachlorophenyliminoquinone does not dissolve in sulphuric acid with the indigo or magenta coloration of the nitroamine from which it is formed; its solution is rather of a red or reddish-brown colour with no trace of blue tint. Moreover, other nitroamines, which are capable of passing into isomeric nitroanilines, also give solutions in sulphuric acid having a magenta or purple colour, whilst the corresponding nitroanilines with sulphuric acid yield colourless, insoluble sulphates and pale yellow solutions. It would seem, therefore, probable that analogous substances were present in the sulphuric acid solution of both classes of nitroamines. In one case, on adding water, the nitroanilines are formed, and in the other, where the production of the nitroaniline is only possible by replacement of halogen by the nitro-group, the phenyliminoquinone is the final product.

It was previously suggested that an iminoquinone was this intermediary stage, and was present as a salt in the coloured acid solution; thus, the conversion of 1-nitroamino-2 : 6-dibromobenzene into 2 : 6-dibromo-4-nitroaniline may be represented as follows:

$NH{\cdot}NO_2$ (Br, Br) → $NH(HSO_4)$ (Br, Br; H, NO_2) → NH_2 (Br, Br; NO_2).

The isolation of the phenyliminoquinone from the coloured acid solution is in harmony with this suggestion. Further, the transference of the chlorine atom from its original position in the nitroamine to the neighbouring carbon atom finds analogy in the reactions of other quinone derivatives. Thus, Kastle (*Amer. Chem. J.*, 1902, **27**, 31) has observed the transformation of *s*-tribromophenol bromide into tetra-

bromophenol, and Auwers (*Ber.*, 1902, **35**, 455) has described the conversion of cyclic nitroketones into nitrophenols.

The following observations may be cited as bearing on this point. In the oxidation of 2 : 6-dibromo-*p*-phenylenediamine by bromine in ethereal solution, Jackson and Calhane (*Amer. Chem. J.*, 1904, **31**, 209) have obtained highly coloured (green) salts of a dibromo-base, which they believe to be a dibromoquinonedi-imine. Schmidt and Saager (*Ber.*, 1904, **37**, 1679) have also prepared by oxidation of tolylenediamine the violet hydrochloride of a base which is thought to be toluquinoneimine. Willstätter (*Ber.*, 1904, **37**, 1494), on the other hand, has described a quinoneimine and a quinonedi-imine (prepared from *p*-aminophenol and *p*-phenylenediamine respectively) which are colourless and form colourless salts. The highly coloured substances may not be simple iminoquinones, but nearly related compounds, possibly analogous to the intensely coloured quinhydrones.

The phenyliminoquinone cannot be obtained from *s*-trichloroaniline and trichloroquinone under the conditions in which it is produced from the nitroamine, nor from the nitroamine and the trichloroquinone. These facts again suggest that either the nitroamine or the aniline produced from the nitroamine by hydrolysis reacts with an iminoquinone formed in the manner suggested.

Bamberger (*Ber.*, 1902, **35**, 3697) has recorded a number of colour reactions given by chloro- and bromo-anilines when their solutions in concentrated sulphuric acid are treated with a drop of nitric acid or of a sodium nitrite solution. These colours closely resemble those given by the nitroamines in sulphuric acid solution. We have found that the purple solutions thus obtained from *s*-trichloroaniline yielded, when poured on to ice, a red solid, which resembled very closely that obtained from the nitroamine. The mother liquor contained a diazonium salt, ammonia, and a considerable amount of chloride. The red solid, however, did not appear to be homogeneous, although it had the general properties of a phenyliminoquinone, and when treated with sulphuric acid yielded *s*-trichloroaniline.

The study of other similarly constituted nitroaminobenzenes is being continued.

Experimental.

Preparation of 1-*Nitroamino*-2 : 4 : 6-*trichlorobenzene*,

$NH{\cdot}NO_2$

Cl ⟨ ⟩ Cl

Cl

This substance is readily prepared in quantity from *s*-trichloroaniline. Fifty grams of the substituted aniline are dissolved in 450 c.c. of

glacial acetic acid, and 36—40 c.c. of nitric acid (90—95 per cent.), which has been carefully freed from nitrous acid by addition of solid urea nitrate,* added. The solution is then cooled to about 12° and 30 c.c. of acetic anhydride slowly added. The solid trichloroaniline nitrate which has separated gradually dissolves, the liquid assuming a pale red colour. The mixture is now poured on to 600 grams of ice and water, when a copious buff precipitate of the nitroamine appears. The solid is collected, washed with water, and dissolved in a solution of sodium carbonate in order to remove a very small quantity of an insoluble red substance. The nitroamine is again precipitated with hydrochloric acid, washed, and dried at a low temperature. This nitroamine is stable and can be easily kept without any special precautions, but in time it becomes faintly coloured and smells slightly of nitrous fumes.

Interaction of 1-*Nitroamino*-2 : 4 : 6-*trichlorobenzene with Sulphuric Acid.*—This nitroamine dissolves as do other highly substituted nitroaminobenzenes in concentrated sulphuric acid, giving a purple or violet solution, which, in the presence of a small quantity of water, assumes a magenta tint. If the solution is allowed to become warm, or water added, and consequently heat developed, the colour entirely disappears. When the coloured solution in sulphuric acid is poured on to ice, a red solid is precipitated which is, however, not homogeneous, but probably a mixture of chlorophenyliminoquinones. The liquid contains mainly a diazonium salt, but at the same time both chloride and ammonia are present. The solution, which has been rendered colourless by heating, yields on dilution with water a solid product in which chloroanil and *s*-trichloroaniline can be recognised; both chloride and ammonia are present in the aqueous liquor.

Preparation of s-*Trichlorophenyliminotrichlorobenzoquinone*,

Cl Cl Cl
Cl⟨ ⟩·N:⟨ ⟩:O·
Cl Cl

When the action of sulphuric acid on the nitroaminotrichlorobenzene is moderated by dilution with acetic acid, a single product, *s*-trichlorophenyliminotrichlorobenzoquinone, can be isolated.

Two grams of the nitroamine are dissolved in 40 c.c. of glacial acetic acid (it is essential that the acetic acid should not contain more than 1—2 per cent. of water), and a solution of 20 c.c. of concentrated sulphuric acid in 20 c.c. of glacial acetic acid is slowly added; the

* The addition of urea nitrate forms a very convenient method of removing the last traces of nitrous acid without materially diluting the nitric acid; a small quantity of ammonium nitrate remains in the nitric acid.

temperature is so regulated that the acetic acid begins to solidify. A deep indigo coloration develops, but if water is present in the sulphuric or acetic acid only a red or magenta coloration is seen. Any evolution of nitrous fumes points to a too rapid addition of sulphuric acid. The mixture is now allowed to stand for twenty minutes, and then poured on to ice, when the colour disappears and a red solid is precipitated. This solid consists mainly of the iminoquinone mixed with a varying amount of unchanged nitroamine, which is removed by extraction with dilute sodium carbonate solution. The red solid is washed and dried, and purified by recrystallisation from dilute acetone, or, better, from petroleum (b. p. 80—100°). From the former solvent it separates in bronze-red, flattened needles, and from the latter in deep red prisms melting at 143°. It sublimes at 225—240° under 40 mm. pressure. It dissolves very readily in chloroform, benzene, or acetone, is fairly soluble in acetic acid, and sparingly in alcohol or petroleum; from the latter, it crystallises exceedingly well. On analysis, the following numbers were obtained:

0·1250 gave 0·1697 CO_2 and 0·0132 H_2O. C = 37·02; H = 1·1.
0·1514 ,, 0·2020 CO_2 ,, 0·0168 H_2O. C = 36·39; H = 1·23.
0·241 ,, 8·2 c.c. of moist nitrogen at 20° and 773 mm. N = 3·92.
0·1748 ,, 0·3855 AgCl. Cl = 54·52.
0·186 dissolved in 8·8 grams of benzene gave Δt = 0·266°. M. W. = 389.
$C_{12}H_3ONCl_6$ requires C = 36·93; H = 0·78; N = 3·6; and Cl = 54·54 per cent., M. W. = 389·77.

Recognition of other Products of Decomposition of the Nitroamine.

The diazonium salt could be easily recognised in the acid filtrate obtained in the preparation of this red solid either by coupling with β-naphthol or by warming with alcohol; in the latter case, *s*-trichlorobenzene, melting at 65°, crystallised out. The amount of the diazo-compound was estimated by slowly adding an aliquot part of the filtrate to a cooled 10 per cent. solution of sodium hydroxide, the latter being in sufficient amount to neutralise the acid; no precipitate is formed in this process. A solution of β-naphthol in a few c.c. of sodium hydroxide is then introduced, and the alkalinity diminished by carbon dioxide. The orange precipitate is collected and washed with water and alcohol.

s-*Trichlorobenzeneazo-β-naphthol*,

$N_2 \cdot C_{10}H_6 \cdot OH$

Cl Cl

Cl

This substance, which was also prepared from *s*-trichlorobenzenediazonium hydrogen sulphate and β-naphthol, crystallised from glacial acetic acid in scarlet needles melting at 145—146°.

0·209 gave 14·8 c.c. moist nitrogen at 15° and 755 mm. N = 8·24.
$C_{16}H_9ON_2Cl_3$ requires N = 7·9 per cent.

The amount of azo-derivative found corresponded to about 55—60 per cent. of the nitroamine decomposed.

The ammonia was estimated in the filtrate from the coupled product. The liquid was acidified and evaporated to dryness; the ammonia was then distilled off and estimated. One molecular proportion of ammonia was found for each gram-molecule of phenyliminoquinone.

Decomposition of the Hexachlorophenyliminoquinone with Sulphuric Acid.—The phenyliminoquinone dissolves in sulphuric acid to a reddish-brown solution. On adding water, without cooling, the colour is partly discharged, and on adding more water golden-yellow crystals at first and later colourless needles separate. On diluting the sulphuric acid solution with acetic acid or alcohol, the colour is also discharged, but no crystals appear.

One gram of the quinone is dissolved in 15 c.c. of sulphuric acid and 30 c.c. of water gradually added; on cooling the hot liquid, yellow crystals separated. The whole of the solid when precipitated by water weighed 0·92 gram; it was treated with cold alcohol, which left a residue of small, yellow plates weighing 0·4 gram. From the alcoholic extract, colourless needles were precipitated by water, weighing 0·44 gram; they melted at 76°, the melting point of *s*-trichloroaniline, and did not lower the melting point of this substance. When acetylated with acetyl chloride in acetic acid solution, they gave *s*-trichloroacetanilide, melting at 202°.

The golden-yellow plates melted at 157—158°, and after two crystallisations from hot alcohol, constantly at 163°. This substance was soluble in and decomposed by sodium hydroxide. An estimation of the chlorine gave the following numbers:

0·1136 gave 0·2299 AgCl. Cl = 50·04.
Trichloroquinone, $C_6HO_2Cl_3$, requires 50·32 per cent.

A specimen of trichloroquinone was prepared by oxidising phenol with potassium chlorate and hydrochloric acid, and freed from chloranil by conversion into the corresponding quinol (Knapp and Schultz, *Annalen*, 1881, **210**, 174). A mixture of the two specimens melted at 163—164°.

Attempts to prepare this quinone directly from the nitroamine by prolonged treatment of the solution in glacial acetic acid with sulphuric acid, or by heating the material in acetic acid solution with sulphuric acid, gave, besides *s*-trichloroaniline, a mixture of quinones, from which tetrachloroquinone, chloranil, could always be isolated. *s*-Trichlorobenzene was also detected, produced probably by the decomposition of *s*-trichlorobenzenediazonium salt. At the same time, chlorine was always found in the mother liquors.

Reduction of the Trichlorophenyliminotrichlorobenzoquinone. s-*Trichlorophenyl*-2 : 3 : 6-*trichloro*-4-*hydroxyphenylamine.*

Cl Cl Cl
Cl<⬡>·NH·<⬡>·OH.
Cl Cl

The hexachlorophenyliminobenzoquinone (2 grams) was dissolved in acetone and an equal weight of zinc dust added. Glacial acetic acid was run in drop by drop until the solution became colourless. After filtering and adding water, a colourless solid separated, which was recrystallised from petroleum (b. p. 80—100°). It forms long, silky, white needles melting at 186°; it is very soluble in benzene, chloroform, ether, or acetone, but less so in alcohol. It dissolves in aqueous and more readily in alcoholic alkali hydroxides.

0·1464 gave 0·1950 CO_2 and 0·0240 H_2O. C = 36·33 ; H = 1·82.
0·1521 ,, 0·2020 CO_2 ,, 0·021 H_2O. C = 36·23 ; H = 1·52.
0·2516 ,, 8·2 c.c. of moist nitrogen at 13·5° and 775 mm. N = 3·89.
0·1797 ,, 0·3906 AgCl. Cl = 53·76.
0·1729 ,, 0·3771 AgCl. Cl = 53·92.
$C_{12}H_5ONCl_6$ requires C = 36·75 ; H = 1·29 ; N = 3·58 ; Cl = 54·27 per cent.

The diphenylamine derivative could be readily oxidised in benzene solution by mercuric oxide to the original hexachlorophenyliminoquinone (m. p. 143°).

Benzoyl Derivative.—The diphenylamine derivative (0·5 gram) was dissolved in 3 c.c. of pyridine and excess (0·25 c.c.) of benzoyl chloride added; after 24 hours, the liquid was poured into dilute sulphuric acid and the solid which separated washed successively with water, aqueous sodium carbonate, and alcohol. From alcohol, it crystallises in small,

lustrous prisms melting at 169°. It was insoluble in aqueous sodium hydroxide, and analysis showed that it was a monobenzoyl derivative.

0·094 gave 0·1627 AgCl. Cl = 42·80.
$C_{19}H_9O_2NCl_6$ requires Cl = 42·90 per cent.

Comparison of the Behaviour of 1-*Nitroamino*-s-*trichlorobenzene on Treatment with Sulphuric Acid with that of* 1-*Nitroamino*-2 : 6-*dibromo- and* 1-*Nitroamino*-2 : 4-*dichloro-benzene.*

1-*Nitroamino*-2 : 6-*dibromobenzene*,

$NH{\cdot}NO_2$
Br / \ Br
| |
\ /
.

1-Nitroamino-2 : 6-dibromobenzene can be readily prepared from 2 : 6-dibromoaniline in the same manner as the *s*-trichloro-derivative, and thus offers a marked contrast to the 2 : 4-dichloro-derivative (compare Trans., 1902, **81**, 812). It crystallises from water in long needles melting at 108° and becoming coloured at 110°; it resembles the *s*-trihalogen derivatives very closely.

0·2012 gave 0·2572 AgBr. Br = 54·43.
$C_6H_4O_2N_2Br_2$ requires Br = 54·58 per cent.

When a solution of this nitroamine (0·5 gram) in glacial acetic acid (10 c.c.) was treated with a solution of sulphuric acid (5 c.c.) in acetic acid (5 c.c.), a magenta coloration appeared. On pouring this mixture on to ice, a yellow precipitate was formed, which weighed about 0·4 gram and was nearly pure 2 : 6-dibromo-4-nitroaniline. The filtrate contained no bromide, but coupled with β-naphthol; diazonium salt was therefore present, but only in very small amount.

When 1-nitroamino-2 : 4-dichlorobenzene was treated in the same manner, the isomeric nitroaniline, 2-nitro-4 : 6-dichloroaniline, was the main product, a very small amount of diazonium salt being formed at the same time. In the case of both the nitroamines above mentioned, there was no indication of the presence of a phenyliminoquinone as one of the products of the reaction.

The authors wish to express their indebtedness to the Chemical Society for the grant from the Research Fund, which has partly defrayed the expenses of this investigation.

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XLIX.—*The Constituents of Gambier and Acacia Catechus. II.*

By Arthur George Perkin, F.R.S.

The question as to the identity of the catechins which exist in acacia and gambier catechus has long remained uncertain, but in a recent communication (Trans., 1902, **81**, 1160) strong evidence was given to show that although the general reactions of these substances are the same, they are, however, distinct compounds. It was found, for instance, that air-dried acacia catechin has the formula $C_{15}H_{14}O_6,3H_2O$ and melts at 203—205°, whereas gambier catechu contains two catechins, namely, $C_{15}H_{14}O_6,4H_2O$ (m. p. 175—177°) and $C_{15}H_{14}O_6$? (anhydrous), melting at 235—237°. These distinctions were further enhanced by an observation of the melting points of certain of their derivatives. In a later investigation by Clauser (*Ber.*, 1903, **36**, 101) on this subject, no reference is made to the above-mentioned work, and his results suggest that there is but one catechin, and that this, according to the amount of water of crystallisation which is present, exists in three well-defined modifications. The catechin he employed was obtained from gambier catechu (Wurfel catechu), and to this substance when dried in the air he assigned the formula $C_{15}H_{14}O_6,4H_2O$, in agreement with the results previously described (*loc. cit.*) and with those of Kostanecki and Tambor (*Ber.*, 1902, **35**, 1867). This compound melts at 96°, and when dried over sulphuric acid loses $3H_2O$ and melts at 176°; finally, on drying at 100°, it is obtained in the anhydrous condition and melts at 210°. The first two of these results do not require comment, for it is a common experience that air-dried gambier catechin which has been crystallised from water will liquefy in the steam oven, and, again, the melting point (176°) for the compound $C_{15}H_{14}O_6,H_2O$ coincides with that found for the anhydrous substance. The statement, however, that in the latter condition gambier catechin melts at 210° was difficult to understand, and especially so as this was near to the melting point, 203—205°, of acacia catechin, and was suggestive in this respect. In the present communication, these points are discussed and further compounds derived from both catechins are described. For a plentiful supply of acacia catechu (kath), I am indebted to the authorities of the Imperial Institute.

Experimental.

Experiment corroborated the work of Clauser in that air-dried gambier catechin, $C_{15}H_{14}O_6,4H_2O$, melts at 96°, and that this, after

standing over sulphuric acid, has the formula $C_{15}H_{14}O_6,H_2O$ (found, $H_2O = 5{\cdot}72$ per cent.) and melts at 175—177°. It was found, however, that when dried at 100° the substance still melted at 175—177° as previously stated, in that at this temperature the colourless crystals had congealed together to form viscous globules. To be certain that the compound at this temperature was fused, a small quantity was heated in a test-tube under similar conditions, and on inserting a glass rod there could be no doubt that the product had a treacly consistency. On further heating, the substance underwent no apparent alteration until about 205°, when decomposition ensued with the usual frothing, and it is evident that it was this action which Clauser regarded as the true melting point of the gambier catechin.

Air-dried acacia catechin, $C_{15}H_{14}O_6,3H_2O$, on the other hand, sintered at about 140°, resolidified as the temperature rose, and finally melted with decomposition at 203—205°.

As previously observed, the anhydrous substance melts at 203—205°. To avoid confusion, the term *Acacatechin* will now be applied to the latter substance, and the name *Catechin* retained for that occurring in gambier, for the latter product is better known and more largely employed than the other variety.

As an acetylacacatechin had not been previously obtained, it was interesting to prepare such a compound in order to compare it with the acetylcatechin first described by Liebermann and Tauchert (*Ber.*, 1880, **30**, 964) and subsequently examined by Kostanecki and Tambor (*Ber.*, 1902, **35**, 1867). In this case, acetylation by the ordinary process is not satisfactory, but the pyridine method gives good results when 2 grams of substance, 30 grams of pyridine, and 10 grams of acetyl chloride are employed. The product was treated with water and the viscous residue crystallised two or three times from a mixture of acetone and alcohol.

Found, $C = 60{\cdot}32$, $59{\cdot}99$; and $H = 4{\cdot}42$, $4{\cdot}72$.

$C_{15}H_9O_6(C_2H_3O)_5$ requires $C = 60{\cdot}00$; $H = 4{\cdot}80$ per cent.

It formed colourless needles melting at 158—160°, sparingly soluble in alcohol. The percentage of acetyl groups was determined by the ethyl acetate method (Trans., 1905, **87**, 107).

Found, acetic acid = 60·18. Theory for 5 acetyls requires 60 per cent.

It was therefore a *penta-acetyl* derivative.

The acetylcatechin first described by Liebermann and Tauchert and referred to above melts at 124—125°, and although these authors do not state the source of their product it would appear to be gambier catechin. To be certain on the point, a quantity of this substance was acetylated by the pyridine method, and the product was found to possess

identical properties to the compound described by these authors. Found, acetic acid = 60·24 per cent. *Penta-acetylacacatechin* is, therefore, not identical with acetyl catechin.

The methylation of acacatechin was now studied, and to prepare this a solution of the substance in methyl alcohol was treated in the usual way with molecular proportions of methyl sulphate and potassium hydroxide until a colour change was no longer produced in the liquid by the action of the latter. Addition of water caused the separation of a colourless precipitate, which was collected, washed with dilute alkali, and drained on tile; this product was first crystallised two or three times from alcohol, by which a more soluble substance was removed, and finally from acetone until the melting point was constant.

Found, C = 66·03, 65·84; H = 5·95, 6·57; OCH_3 = 34·87 per cent.
$C_{15}H_{10}O_2(OCH_3)_4$ requires C = 65·89; H = 6·36; OCH_3 = 35·83 per cent.

Acacatechin tetramethyl ether forms colourless needles melting at 152—154°, sparingly soluble in cold alcohol, insoluble in aqueous alkaline solutions; it crystallises from alcohol in prisms which contain alcohol of crystallisation, and as this is somewhat troublesome to remove completely the purification of the compound by means of acetone is preferable. When a solution of this compound in acetic acid is treated with a few drops of nitric acid, a deep indigo-blue coloration is produced, which is permanent for several hours. The more soluble product of the methylation above referred to was not critically examined, but it seems probable that this may contain the acacatechin pentamethyl ether.

To be certain that the tetramethyl derivative contains a free hydroxyl group, it was digested with acetic anhydride and sodium acetate in the usual manner. The colourless product of the reaction was purified by crystallisation from alcohol.

Found, C = 64·83; H = 6·44.
$C_{15}H_9O_2(C_2H_3O)(OCH_3)_4$ requires C = 64·94; H = 6·18 per cent.

Monacetylacacatechin tetramethyl ether separates in long needles which melt at 135—137° and are sparingly soluble in alcohol.

According to Kostanecki and Tambor (*loc. cit.*), catechin tetramethyl ether melts at 142—143° and its acetyl compound at 92—93°, temperatures which are considerably lower than those exhibited by the acacatechin derivatives. For purposes of comparison, a small quantity of Kostanecki and Tambor's compound was prepared, and this, on repeated crystallisation from acetone, melted at 144—146°, or slightly higher than is stated by these authors. In other respects, this substance closely resembled the acacatechin derivative, and, it is interesting to note, gives with nitric and acetic acids the same indigo-blue liquid.

It is, however, evident that the tetramethyl ethers of catechin and acacatechin are distinct substances.

Oxidation with Potassium Permanganate.—Acacatechin tetramethyl ether, made into a thin cream with water, was heated on the water-bath and treated with a strong solution of the permanganate in small quantities at a time until the red colour of the supernatant liquid remained permanent, the operation requiring about two hours. The excess of permanganate was then destroyed with sodium sulphite, the mixture filtered by means of the pump, and the residue well washed with boiling water. The colourless filtrate was neutralised with acid and extracted with ether, and the extract evaporated. The crystalline residue consisted chiefly of an acid, but a small quantity of a phenolic substance was also present, and these were separated with sodium hydrogen carbonate in the usual manner. The acid crystallised from water in colourless needles melting at 178—180°.

Found, C = 59·32 ; H = 5·48 per cent.

$C_6H_3(OCH_3)_2 \cdot CO_2H$ requires C = 59·34 ; H = 5·49 per cent.

It had all the properties of *veratric acid*, and this was interesting, as it clearly proves that in acacatechin the catechol hydroxyls exist in the free condition.

The phenolic product of the oxidation was obtained as a colourless, semicrystalline mass, but in too small quantity to be identified with certainty. Its alkaline solution, when treated with diazobenzene chloride, gave an orange-yellow precipitate, suggesting that the original substance was *phloroglucinol dimethyl ether*, because had phloroglucinol monomethyl ether been present, an orange-red diazobenzene derivative would have been produced. Attempts to prepare larger quantities of this compound have been unsuccessful, and it is therefore probably itself somewhat susceptible to oxidation by permanganate. For purposes of comparison, catechin tetramethyl ether was treated in a similar manner, with the result that it also yielded *veratric acid* and *phloroglucinol dimethyl ether.*

The action of chromic acid on both compounds was also studied, but in this case only veratric acid could be isolated.

It has been shown by Kraut and Delden (*Annalen*, 1863, **28**, 290) and by Etti (*Annalen*, 1877, **186**, 332) that catechin yields, by treating its solution with acids and by other methods, four distinct amorphous products which are termed "anhydrides." To these reddish-brown substances, the following respective formulæ have been given: $C_{21}H_{18}O_8$, $C_{42}H_{34}O_{15}$, $C_{21}H_{16}O_7$, and $C_{42}H_{30}O_{13}$, and the first or most soluble is said to be identical with catechutannic acid, which exists in the plant side by side with the catechin. The fourth anhydride, named "katechuretin," is insoluble in all solvents and is not dissolved by

alkaline solutions, and it appeared interesting to prepare from both catechins such a compound in case some further distinction between these two substances would be thus detected. An anhydride of this nature, but apparently distinct in composition from those enumerated above, is readily formed from acacatechin by the action of hydrochloric acid in the presence of acetic acid, but a more rapid method consists in adding a few drops of sulphuric acid to the boiling liquid. A bright orange-red powder almost immediately separates, and this is collected at the pump, well drained from the dark-coloured mother liquor, washed with acetic acid, and finally several times with boiling alcohol. On drying at 100°, the product became duller in colour.

(At 160°) Found, C = 63·26 ; H = 3·89 per cent.

This compound does not possess a melting point. Dried at 100°, it retains alcohol or water with remarkable tenacity, and prolonged heating at 160° is necessary to obtain it in the anhydrous condition.

Catechin reacts in an identical manner with hydrochloric or sulphuric acid in the presence of acetic acid. The specimen analysed was prepared with hydrochloric acid.

(At 160°) Found, C = 63·33 ; H = 3·94 per cent.

This substance has similar properties to the acacatechin product, and as the percentage compositions of both are practically identical, they may in fact consist of one and the same substance. It would be useless to speculate on the probable formulæ of these "anhydrides," for their insoluble nature and general properties indicate that they possess a high molecular weight; moreover, their bright orange-red colour and the fact that during their preparation dark soluble products are always formed suggest that the reaction is a complicated one, and not to be regarded as the effect of the mere withdrawal of water. The above analyses are not in accord with those given by Kraut and Delden, who obtained their substance by passing hydrochloric acid into an alcoholic solution of catechin, or with those of Etti, who employed hydrochloric acid in a sealed tube at 160—180°. That the foregoing compound is a pure product seems certain, and it appears to be characteristic of the catechins, for the closely allied cyanomaclurin by a similar method gives an orange-red insoluble anhydride of almost identical composition.

Found, C = 63·48 ; H = 3·94 per cent.

Oxidation with Potassium Ferricyanide.—As is well known, catechin is not to be regarded as a dyestuff, and the tinctorial effects derived from it are assumed to be due to a substance named japonic acid, produced by the oxidation of catechin or catechutannic acid during the

dyeing operation (Hummel and Brown, *J. Soc. Chem. Ind.*, 1896, 15, 422). This substance is only known in the form of the lake, containing both copper and chromium as produced on the fibre, although Schützenberger and Rack (*Bull. Soc. chim.*, 1865, [ii], 4, 5) obtained a dark-coloured insoluble compound, $C_{21}H_{14}O_{10}$, by boiling a catechin solution with potassium dichromate, which is no doubt related to this product.

If a cold aqueous solution of either catechin or acacatechin (5 grams) is treated with potassium ferricyanide (10 grams) no reaction takes place, but if an alkali acetate (10 grams) is then added to the mixture an orange-coloured precipitate is quickly deposited. After standing for half an hour, the product was collected and washed with water, and in this condition closely resembled an alizarin paste. It was drained on porous tile and allowed to dry at the ordinary temperature, for at 100° in the wet condition it congealed to resinous lumps, although when air-dried it is unaffected at this temperature. Thus obtained, it forms an orange-red powder, easily soluble in hot alcohol, and is dissolved by alkaline solutions with an orange-brown coloration. Alcoholic potassium acetate gives an amorphous, reddish-brown potassium salt. Unfortunately, up to the present all attempts to crystallise or to obtain crystalline derivatives from this substance have been unsuccessful. Its chief interest, however, lies in the fact that it is a new colouring matter, for it dyes mordanted calico, preferably in the presence of chalk or calcium acetate, orange-brown shades which are fairly fast to soap. It was at first considered possible that this substance consisted of the japonic acid above referred to in the free state, but attempts to produce the shade given by the latter on fabrics mordanted with copper and chromium did not give the expected result, as the colour was not only of a poorer character, but it possessed a much more orange tint. It seems more probable, therefore, that this dyestuff is related to the catechone of Kostanecki and Tambor (*loc. cit.*), which they obtained in the form of its trimethyl ether, $C_{18}H_{18}O_7$, by oxidising catechin tetramethyl ether with chromic acid in the presence of acetic acid, and which crystallises in orange-coloured needles. As methylation by means of methyl sulphate did not, however, yield a product susceptible of crystallisation, this could not be decided, but the matter is reserved for further study.

Experiments with catechutannic acid showed that in this respect it behaves in an analogous manner to catechin and acacatechin, although in this case the oxidation product is of a more sparingly soluble nature.

Solutions of the catechins in aqueous potassium or sodium hydroxide rapidly darken when exposed to air, owing to oxidation. When, however, they are suspended in water through which a current of carbon

dioxide is passing, and excess of alkali is added, the solution remains colourless, and if the passage of the gas is then continued crystals of unaltered catechin or acacatechin thus separate.

Acacatechin tetramethyl ether is but slowly attacked when heated with alcoholic potash at 180°. Thus, after two hours at this temperature, a considerable quantity was recovered possessing the correct melting point, and in this respect it therefore differs considerably from the ethers of the flavone and flavanol class.

During this work, the possibility suggested itself that acacatechin might be represented as $C_{15}H_{12}O_6$, but this cannot be the case, as after long exposure at 160° its percentage composition was unaltered (found, C = 62·05 ; H = 4·94). There can therefore be no longer any doubt, in view of the numerous results to this effect, that the formulæ of acacatechin and catechin are identical.

Summary of Results.

That catechin and acacatechin are distinct substances is at once evident on comparing the melting points of their corresponding derivatives.

*Penta-acetylcatechin ...	124—125°	*Catechin tetramethyl ether	144—146°
Penta-acetylacacatechin	158—160	Acacatechin tetramethyl ether..	152—154
Pentabenzoylcatechin ...	151—153	*Acetylcatechin tetramethyl ether	92—93
Pentabenzoylacacatechin	181—183	Acetylacacatechin tetramethyl ether	135—137
Azobenzenecatechin.. ...	193—195	Acetylazobenzenecatechin.........	253—255
Azobenzeneacacatechin .	198—200	Acetylazobenzeneacacatechin	227—229

* Kostanecki and Tambor, *loc. cit.*

On the other hand, as previously discussed, the two catechins are so similar in their behaviour with the ordinary reagents that no doubt can be entertained as to their intimate relationship.

The formation of veratric acid and phloroglucinol dimethyl ether by the oxidation of the catechin tetramethyl ethers has determined the position in each case of four of the five necessary hydroxyls, but further information is required before it will be possible to ascertain with certainty the constitution of these compounds. In the former communication, it was suggested as likely that catechin or acacatechin might be regarded as a reduction product of quercetin, thus :

O OH
OH CH——— OH,
CH·OH
OH CH_2

and on this assumption the isomerism existing between these two

compounds could be explained by an alteration in the position of the alcoholic group,

O OH

OH CH- OH,

CH_2

OH CH(OH)

for this rearrangement should have but little effect on the properties of the compound.

It was previously pointed out that the property of giving the phloroglucinol reaction so characteristic of the catechins is not possessed by the corresponding flavone derivatives, and it appeared necessary that in order to be capable of this effect all three hydroxyls of the nucleus must exist in the free condition. Adopting this view, catechin might be regarded as a reduced chalkone derivative :

OH OH OH

$-CO\cdot CH_2\cdot CH_2-$ OH ;

OH

but it is more probable that the effect produced is due in the first place to a hydrolysis by the acid, by which means the third phloroglucinol hydroxyl is liberated.

Experiments were carried out in the hope of isolating a sufficient quantity of the catechin of higher melting point (235—237°) for complete characterisation. The results, possibly due to the substance employed, have been disappointing, and but little over a gram of this substance could be obtained, but a further search is in progress which, it is anticipated, will give larger amounts of this somewhat rare material.

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L.—*Preparation and Properties of 1 : 4 : 5-Trimethylglyoxaline.*

By Hooper Albert Dickinson Jowett.

In previous papers on the constitution of pilocarpine (Trans., 1903, 83, 438), it was shown that this alkaloid must be regarded as a glyoxaline derivative, and, furthermore, that the lower members of

the series, for example, 1:4- (or 1:5-) and 1:2-dimethylglyoxalines, did not possess the physiological action of pilocarpine. It was therefore thought desirable to attempt the preparation of glyoxalines containing acidic groups analogous to the homopilopic complex in pilocarpine by condensing a suitable bromoglyoxaline with substances such as ethyl sodiomalonate. The only bromo-derivative of glyoxalines of the type $\begin{matrix} R'\cdot C\cdot N(CH_3) \\ \| \quad\quad \\ H\cdot C\text{———}N \end{matrix} \!\!>\! CH$ which has been prepared is a dibromodimethylglyoxaline (Jowett and Potter, Trans., 1903, **83**, 466), monobromo-derivatives not having been obtained. It may be noted that only the dibromo-derivatives of pilocarpine and *iso*pilocarpine have been prepared. The only monobromoglyoxalines available would thus appear to be of the type $\begin{matrix} R'\cdot C\cdot N(CH_3) \\ \| \quad\quad \\ R''\cdot C\text{———}N \end{matrix} \!\!>\! CBr$, which, if condensed with aliphatic sodium derivatives, would yield bases differing, however, from pilocarpine in the point of attachment of the acidic complex. It was decided to attempt the preparation of 2-bromo-1:4:5-trimethylglyoxaline as the most suitable substance for the purpose of condensation.

1:4:5-*Trimethylglyoxaline* was prepared from 4:5-dimethylglyoxaline, which had previously been obtained by Künne (*Ber.*, 1895, **28**, 2039). It is a crystalline base, yielding a series of crystalline salts, which were prepared and characterised. On bromination, the desired *monobromotrimethylglyoxaline* was obtained. It is a crystalline base forming crystalline salts which have been prepared and characterised. In this respect, it differs from dibromopilocarpine and dibromo*iso*pilocarpine, which possess only feeble basic properties (Trans., 1901, **79**, 586). Although the required bromoglyoxaline has been obtained, the yield, unfortunately, was so small that it was not considered practicable to prepare sufficient material for the experiments above mentioned. The amount of bromotrimethylglyoxaline obtained from one kilogram of methyl ethyl ketone under the best conditions was only two to three grams. All attempts to improve this yield having failed, it is intended to attack the problem from another standpoint.

Experimental.

1:4:5-*Trimethylglyoxaline*, $\begin{matrix} CH_3\cdot C\cdot N(CH_3) \\ \| \quad\quad \\ CH_3\cdot C\text{———}N \end{matrix} \!\!>\! CH.$

4:5-Dimethylglyoxaline was prepared from the corresponding mercaptan by treatment with nitric acid, the mercaptan being obtained from methyl ethyl ketone according to the method described by Künne (*loc. cit.*). Despite numerous experiments, the maximum yield of

pure base was only 4 per cent. of the ketone taken. The base distilled at 165° under 10 mm. pressure and melted at 117°, this being the temperature given by Künne. The nitrate, after recrystallisation until the melting point was constant, formed colourless, acicular crystals which fused at 180° with effervescence. Künne gave the melting point as 164°.

Dimethylglyoxaline picrate crystallises in brilliant yellow needles, which, after purification by recrystallisation from hot water and drying at 110°, melt at 196—197°. The picrates of the glyoxalines afford one of the easiest methods of identification of these bases, as they are readily formed, crystallise with facility, and have well defined melting points.

Trimethylglyoxaline is best prepared by the action of sodium methylsulphate on the sodium derivative of dimethylglyoxaline, according to Titherley's general method (Trans., 1901, 79, 401). In conducting this operation, it was found necessary, in order to obtain the best yield, to work with not more than 5 grams of glyoxaline at a time, and to expose as large a surface as possible of the mixed sodium salts to the action of heat. Even under the best conditions, the yield of trimethylglyoxaline was only 32 per cent. of the dimethylglyoxaline taken. The crude product, obtained by extracting the sodium salts with ether and removing the ether by distillation, was fractionated under 20 mm. pressure, when the greater portion distilled at 115—120°, a little unchanged dimethylglyoxaline being recovered from the higher fractions. On redistillation, the greater portion boiled at 117° under 20 mm. pressure and solidified in the receiver to a mass of long, acicular crystals. These were drained on porous earthenware and then dried in a vacuum over sulphuric acid. The crystals melt at 46° and are soluble in all proportions in water, alcohol, or ether. On exposure to the air for only a few seconds they absorb moisture and liquefy.

0·1386 gave 0·3340 CO_2 and 0·1132 H_2O. C = 65·7 ; H = 9·1.
0·0972 ,, 21·6 c.c. nitrogen at 18° and 761 mm. N = 25·2.
$C_6H_{10}N_2$ requires C = 65·5 ; H = 9·1 ; N = 25·4 per cent.

The base has the characteristic odour of the glyoxalines previously described.

Attempts to prepare the base by the action of dimethyl sulphate on dimethylglyoxaline were unsuccessful.

Trimethylglyoxaline nitrate, $C_6H_{10}N_2,HNO_3,H_2O$, separates from its aqueous solution in long, acicular crystals which, after purification by recrystallisation, melt at 46°. It is readily soluble in water or alcohol, but insoluble in ether. When crystallised from alcoholic solution by the addition of ether, the crystals melt indefinitely at

from 50° to 70°, owing to partial dehydration. Owing to the low melting point of the hydrate, the water of crystallisation could not be determined by the ordinary methods. On analysis, the salt (m. p. 46°) gave the following result:

0·149 gave 0·210 CO_2 and 0·0962 H_2O. C = 38·4; H = 7·2.
$C_6H_{10}N_2,HNO_3,H_2O$ requires C = 37·7; H = 6·8 per cent.

Trimethylglyoxaline hydrochloride, $C_6H_{10}N_2,HCl,H_2O$, separates from its aqueous solution in long, acicular crystals which, when dried in the air, melt indefinitely at about 80°, but after drying either in a desiccator over sulphuric acid or at 110°, the crystals melt sharply at 199°. The crystals are freely soluble in water or alcohol, but insoluble in ether.

0·225 air dried salt lost 0·025 at 110°. H_2O = 11·1.
0·20 anhydrous salt gave 0·1954 AgCl. Cl = 24·2.
$C_6H_{10}N_2,HCl,H_2O$ requires H_2O = 10·9.
$C_6H_{10}N_2,HCl$ requires Cl = 24·2 per cent.

The *aurichloride* formed yellow, acicular crystals which, after drying at 110°, melted at 202°.

0·122 gave 0·0536 Au. Au = 43·9.
$C_6H_{10}N_2,HAuCl_4$ requires Au = 43·8 per cent.

The *platinichloride* slowly separated from its aqueous solution as yellow crystals which, after drying at 110°, melted at 224—225°.

0·0926 gave 0·0288 Pt. Pt = 31·1.
$(C_6H_{10}N_2)_2,H_2PtCl_6$ requires Pt = 31·0 per cent.

The *picrate* formed yellow, acicular crystals which, after recrystallisation from hot water and drying at 110°, melted at 218°.

The *methiodide* was prepared by adding methyl iodide to the base, when a violent reaction occurred and the mixture at once solidified. The crystals were recrystallised from alcoholic solution by the addition of ether, and separated in long needles readily soluble in water or alcohol, insoluble in ether, and, after drying at 110°, melted at 158°.

0·189 gave 0·176 AgI. I = 50·3.
$C_6H_{10}N_2,CH_3I$ requires I = 50·4 per cent.

*2-Bromo-*1 : 4 : 5*-trimethylglyoxaline*, $\begin{matrix} CH_3\cdot C\cdot N(CH_3) \\ CH_3\cdot C\text{———}N \end{matrix} \gt CBr$.

Preliminary experiments proved that this substance could not be prepared by methods analogous to those employed in the case of 1 : 4- (or 1 : 5-) dimethylglyoxaline and pilocarpine. It was ultimately obtained by the following method.

Trimethylglyoxaline (2·8 grams) was dissolved in about 10 c.c. of carbon disulphide, and to the solution 4·1 grams of bromine in 10 c.c. of carbon disulphide were gradually added. Considerable heat was evolved and the mixture was kept cool. After a certain quantity of bromine had been added, a crystalline solid, presumably the hydrobromide of the base, began to separate, and this was dissolved by the addition of a little alcohol to the mixture. The solvent was then removed by distillation, the residue dissolved in water, excess of potassium carbonate added, and the alkaline liquid extracted several times with ether. The ethereal solution was then washed and dried, and, after distillation, left a residue which was crystallised from hot water. The best yield of crystalline product obtained was 22 per cent. of the base taken.

Bromotrimethylglyoxaline, $C_6H_9N_2Br,2H_2O$, crystallises from hot water in long, silky needles, which, when dried in the air, melt at 49°, but after drying in a desiccator over sulphuric acid fuse at 83°. It is readily soluble in hot water, alcohol, or ether, but sparingly so in cold water. Its aqueous solution is feebly alkaline, but the base dissolves readily in acids forming salts. It has a characteristic powerful narcotic odour.

0·2880 air-dried lost 0·0480 in a vacuum over H_2SO_4. $H_2O = 16·6$.
$C_6H_9N_2Br,2H_2O$ requires $H_2O = 16·0$ per cent.

The dried base (m. p. 83°) was analysed with the following result:

0·0844 gave 0·0841 AgBr. Br = 42·4.
$C_6H_9N_2Br$ requires Br = 42·3 per cent.

The *hydrobromide* crystallises in hard cubes which are soluble in water or alcohol, but insoluble in ether. When dried at 110°, the crystals melt at 208°.

0·1139 gave 0·1565 AgBr. Br = 58·5.
$C_6H_9N_2Br,HBr$ requires Br = 59·2 per cent.

The *aurichloride* formed yellow, acicular crystals which were sparingly soluble in cold water, but more freely in the hot solvent. After drying at 110°, the crystals melted at 191°.

0·1874 gave 0·0698 Au. Au = 37·2.
$C_6H_9N_2Br,HAuCl_4$ requires Au = 37·2 per cent.

The *picrate* formed yellow, acicular crystals, which, after recrystallisation from hot water and drying at 110°, melted at 173°.

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LI.—*The Velocity of Oxime Formation in Certain Ketones.*

By Alfred Walter Stewart, B.Sc., 1851 Exhibition Scholar of the University of Glasgow.

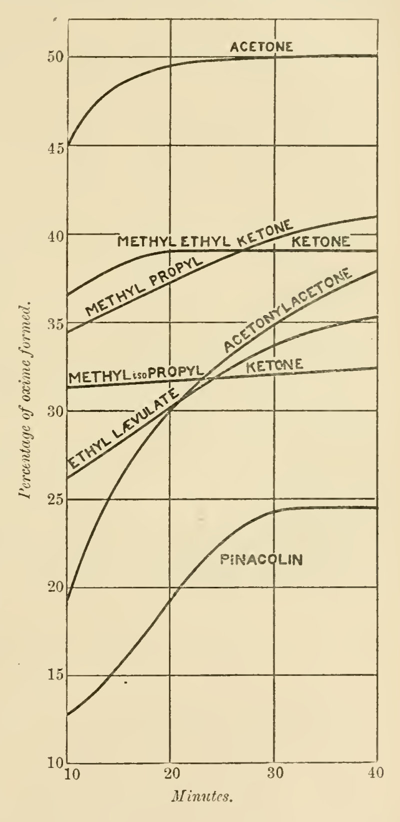
The hindering influence produced by the introduction of various groups into ketonic compounds has been already studied by the author in the case of the additive products formed with sodium hydrogen sulphite (Trans., 1905, **87**, 185), and it seemed desirable to apply a somewhat similar method to the case of oxime formation, with the view of finding whether steric hindrance was actually the chief factor in the problem. If the rates of formation of the oximes of various ketones showed the same relations to each other as those found in the case of the "bisulphite" compounds, the probability that steric hindrance played a great part in the reaction would be increased, since chemically the reactions are quite different in character.

The simplest method of estimating the percentage of oxime formed in a given case seemed to be to determine the amounts of free hydroxylamine present in a solution both before and after the reaction has lasted for a fixed interval of time.

Several series of experiments were carried out before a satisfactory process was discovered. At first an indirect method was tried: a fixed excess of ferric sulphate was boiled with the oxime solution in an atmosphere of carbon dioxide, and the amount of ferrous sulphate thus formed was estimated by titration with potassium permanganate. This did not give concordant results, nor did direct titration of the unchanged hydroxylamine, either with Fehling's solution or with a solution of potassium nitrite.

In the end the following mode of estimation, adapted from a method of estimating hydroxylamine described by Meyeringh (*Ber.*, 1877, **10**, 1940), was found to be the best. In order to obtain results comparable with those already found in the case of the "bisulphite" compounds, $N/10$ aqueous solutions of the ketones were diluted with alcohol to $N/12$. Fifty c.c. of the ketone solution were mixed with an equal volume of $N/12$ hydroxylamine sulphate solution, and the mixture was left in ice. Every ten minutes, 10 c.c. were withdrawn, to which were added 20 c.c. of $N/5$ iodine solution and 20 c.c. of $N/5$ disodium hydrogen phosphate solution; the whole was placed on a water-bath for one minute, and the excess of iodine remaining was then titrated with sodium thiosulphate in the usual way.

The rationale of the method is as follows. The ketone, in forming an oxime, uses up a certain quantity of hydroxylamine; the remaining hydroxylamine is decomposed by warming with the iodine solution, and the hydriodic acid thus produced is taken up by the sodium phosphate before it affects the oxime; the amount of iodine left unchanged is then estimated by means of the thiosulphate titration, and from it the amount of hydroxylamine employed in oxime formation can be deduced. This method was found to be sufficiently accurate, the results being concordant to within one per cent., which is sufficiently close for the purpose in view. It fails, however, when employed with aldehydes, owing to their ready oxidation; and also in the case of compounds containing the group $-CO\cdot CH_2\cdot CO-$ which react with iodine on warming.



The results obtained are shown in the table and curves. In the case of acetonylacetone, twice the usual quantity of the hydroxylamine solution was used, and the results given show the percentage of oxime formed at each carbonyl group.

	10	20	30	40 minutes.	
Acetone	45·1	49·7	50·0	50·1	percentage of oxime
Methyl ethyl ketone	36·6	39·2	39·2	39·2	,, ,,
,, propyl ,,	34·7	37·3	39·9	41·2	,, ,,
,, *iso*propyl ketone	31·4	31·5	32·0	32·0	,, ,,
Ethyl lævulate	26·1	30·0	33·9	35·0	,, ,,
Acetonylacetone	19·0	30·0	35·0	39·0	,, ,,
Pinacolin	12·9	17·0	24·5	24·5	,, ,,

On the whole, the foregoing results appear to support those already obtained as to the influence of the methyl group when it is substituted for a hydrogen atom near the carbonyl group. During the first ten minutes of all the reactions, the only divergence from the relations determined in the case of the "bisulphite" compounds is to be found with ethyl lævulate, the velocity of the "bisulphite" reaction of which lay between those of methyl propyl and methyl *iso*propyl ketones, whilst in the foregoing table it has a lower rate of reaction than methyl *iso*propyl ketone. Apart from this instance, the same influences appear to govern the courses of both reactions. If the percentages of oxime formed by acetone, methyl ethyl ketone, methyl *iso*propyl ketone, and pinacolin at the end of twenty minutes are considered, the following numbers are obtained:

$CH_3{\cdot}CO{\cdot}CH_3$	49·7 per cent.	$CH_3{\cdot}CO{\cdot}CH(CH_3)_2$......	31·5 per cent.
$CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_3$......	39·2 ,,	$CH_3{\cdot}CO{\cdot}C(CH_3)_3$	17·0 ,,

It will be noticed that the velocity of the reaction in the case of methyl ethyl ketone appears to undergo retardation after twenty minutes, causing the percentage of oxime generated at the end of a forty-minute period to fall below that produced in the case of methyl *iso*propyl ketone.

The reaction of oxime formation appears to be, on the whole, more rapid than the addition of sodium hydrogen sulphite to the carbonyl group; a state of equilibrium is reached more speedily. This is to be expected when we take into account the nature of the reaction and the relative masses of the groups involved. In the case of the "bisulphite" compounds it is merely a question of adding on a bulky group:

$$\begin{matrix}R\diagdown\\ \quad\rangle C{:}O\\ R\diagup\end{matrix} + \begin{matrix}SO_3Na\\ |\\ H\end{matrix} = \begin{matrix}R\diagdown\quad\diagup SO_3Na\\ \quad\rangle C\langle\\ R\diagup\quad\diagdown OH\end{matrix},$$

whereas in the second instance a smaller group enters, and water is immediately eliminated:

$$\begin{matrix}R\diagdown\\ \quad\rangle C{:}O\\ R\diagup\end{matrix} + \begin{matrix}NH{\cdot}OH\\ |\\ H\end{matrix} = \begin{matrix}R\diagdown\quad\diagup NH{\cdot}OH\\ \quad\rangle C\langle\\ R\diagup\quad\diagdown OH\end{matrix} = \begin{matrix}R\diagdown\\ \quad\rangle C{:}N{\cdot}OH\\ R\diagup\end{matrix} + H_2O.$$

The oximes appear to be better suited than the "bisulphite" compounds for estimations of the velocity of formation of additive compounds of ketones, when many methyl groups lie in the neighbourhood of the carbonyl. The oxime method has also a great advantage over the other, since in the titration of the "bisulphite" compounds a slow inverse action takes place, which does not occur in the case of the hydroxylamine estimation. This method might

conceivably be useful in confirming the constitutions of cyclic carbonyl compounds containing many methyl groups.

In conclusion, the author wishes to thank Professor Collie and Dr. Smiles for assistance given during the above research.

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LII.—*Limonene Nitrosocyanides and their Derivatives.*

By FREDERICK PEACOCK LEACH.

IN a "preliminary notice of some new derivatives of pinene and other terpenes" (*Proc.*, 1902, **18**, 163), it was shown by Tilden and Burrows that whilst pinene nitrosochloride yields with potassium cyanide a crystalline nitrosocyanide, a mixture of the isomeric limonene nitrosochlorides gives a liquid product.

By modifying the conditions of experiment, it has since been found that the separate limonene nitrosochlorides yield corresponding crystalline nitrosocyanides, the investigation of which I have continued at the request of Professor Tilden.

The following table contains a statement of the principal physical characters of the limonene nitrosochlorides, as determined by Wallach and Conrady, together with those of the new compounds derived from them by processes the details of which will be found in the experimental part of this paper :

Compound.	Dextro- and lævo-, m. p.	Racemic, m. p.	Dextro- $[\alpha]_D$.	Lævo- $[\alpha]_D$.
Limonene (Wallach and Conrady)	—	—	+106·8°	−105·0°
α-Nitrosochloride ,, ,,	103—104°	—	+313·4	−314·8
β-Nitrosochloride ,, ,,	not	definite	+240·3	−242·2
α-Nitrosocyanide	90—91°	81°	+152·7	−152·2
Benzoyl α-nitrosocyanide	108	96	+126·3	−127·2
β-Nitrosocyanide	140—141	159—160	−31·6	+30·6
Benzoyl β-nitrosocyanide	121	98	−108·2	+108·7
α-Amide	138	155	+174·9	−174·0
Benzoyl α-amide	152	150	+241·7	−242·0
α-Carboxylic acid	97	116	+102·9	−103·9
Dihydrocarvoxime	88·5	115	+9·45	−9·25

The α- and β-nitrosochlorides both yield the same two isomeric nitrosocyanides, referred to in this paper as the α- and β-modifications,

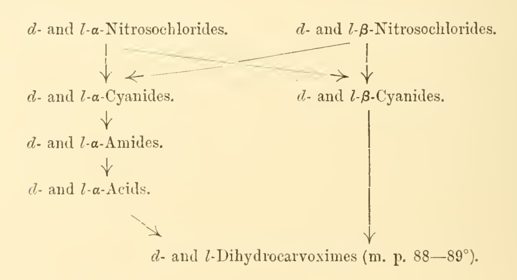
and these two compounds are produced from the α-nitrosochloride in the same proportion as from the β-nitrosochloride. These remarks apply equally to the derivatives of *d*- and *l*-limonenes.

This observation is in accord with the account given by Wallach (*Annalen*, 1889, **252**, 113, and 1892, **270**, 181) of the production of two isomeric nitrolamines from limonene α- and β-nitrosochlorides respectively.

The *d*- and *l*-α-nitrosocyanides behave quite normally as nitriles, giving on hydrolysis the corresponding amides and acids. The acids are characterised by the readiness with which they part with carbon dioxide, yielding the normal oxime of *d*- and *l*-dihydrocarvones.

The β-nitrosocyanides are, however, produced in such small quantity that material sufficient for the preparation of the corresponding amides and acids has not been accumulated, but on hydrolysis with caustic potash these cyanides yield the oximes of dihydrocarvone identical with those obtained from the α-acids.

The following scheme will elucidate the relationship of the new compounds :



In order to discuss the nature of the isomerism of these nitrosochlorides and nitrosocyanides, the formula recently established by W. H. Perkin, jun. (Trans., 1904, **85**, 654), may be assumed.

The α- and β-nitrosocyanides formed from these two nitrosochlorides in the manner already indicated are unimolecular, and their isomerism can only be accounted for on the *cis*- and *trans*-hypothesis, the more fusible isomeride (m. p. 90—91°) being assumed to be the *cis*-compound and the less fusible (m. p. 140—141°) isomeride its *trans*-correlative.

cis

CH_3 CN / C / H_2C C:NOH / H_2C CH_2 / C / CH_3·C H / CH_2 → CH_3 CO·NH_2 / C / H_2C C:NOH / H_2C CH_2 / C / CH_3·C H / CH_2 → CH_3 CO_2H / C / H_2C C:NOH / H_2C CH_2 / C / CH_3·C H / CH_2 ↓

Limonene α-nitrosocyanide (m. p. 90—91°). α-Amide (m. p. 138°). α-Acid (m. p. 97°).

trans

CN CH_3 / C / H_2C C:NOH / H_2C CH_2 / C / CH_3·C H / CH_2 ——→ CH_3 H / C / H_2C C:NOH / H_2C CH_2 / C / CH_3·C H / CH_2

Limonene β-nitrosocyanide (m. p. 140—141°). Dihydrocarvoxime (m. p. 88—89°).

The isomerism of the nitrolamines must be accounted for in a similar way.

A remarkable resemblance exists between the limonene α-nitrosocyanides and their derivatives and the nitrosocyanide prepared by Wallach (*Annalen*, 1888, **248**, 164) from amylene nitrosate.

The acid obtained by hydrolysing the cyanide in each case happens to melt at the same temperature, 97°, and both at this temperature pass into oximes with vigorous evolution of carbon dioxide. As already stated, the limonene α-acid gives the normal oxime of dihydrocarvone, whilst the acid from amylene nitrosocyanide yields the oxime of methyl *iso*propyl ketone, $(CH_3)_2CH\cdot C(NOH)\cdot CH_3$.

The mechanism of the process by which the isomeric nitrosocyanides are formed from the limonene bimolecular nitrosochlorides is not yet fully elucidated, but it may be regarded as probable that at the moment of separation of the two semi-molecules of the nitrosochloride a double link is temporarily formed by the removal of the elements of hydrogen chloride:

$$\left[C_7H_{12} \left\langle \begin{array}{l} C \left\langle \begin{array}{l} CH_3 \\ Cl \end{array} \right. \\ | \\ C \left\langle \begin{array}{l} H \\ NO- \end{array} \right. \end{array} \right. \right]_2 \longrightarrow \left[C_7H_{12} \left\langle \begin{array}{l} C\cdot CH_3 \\ \| \\ C\cdot NO- \end{array} \right. \right]_2$$

This is immediately followed by the addition of hydrogen cyanide, while the bisnitroso-compound changes into the oxime :

$$\left[C_7H_{12}\begin{matrix} \diagup C < \begin{matrix} CH_3 \\ CN \end{matrix} \\ | \\ \diagdown C < \begin{matrix} H \\ NO- \end{matrix} \end{matrix} \right]_2 \quad \longrightarrow \quad 2\left[C_7H_{12}\begin{matrix} \diagup C < \begin{matrix} CH_3 \\ CN \end{matrix} \\ | \\ \diagdown C{:}NOH \end{matrix} \right]$$

whether the *cis*- or *trans*-form of nitrosocyanide is produced would depend, according to this hypothesis, on which of the two bonds temporarily formed is saturated by the addition of the hydrogen cyanide, and it may be supposed that the nitrosocyanide, which is formed in the smaller proportion, namely, the β-compound, would be the product of this succession of changes. The α-nitrosocyanide might be formed in a similar manner, but it appears more probable that this results from the direct substitution of CN for the chlorine of the nitrosochloride. Support is found for the above hypothesis as to the formation of a temporary double linking in the researches of von Baeyer (*Ber.*, 1893, **26**, 2861).

It is noteworthy that whilst the optical activity of the α-nitrosocyanides is in the same sense as that of the nitrosochlorides from which they are derived, the β-nitrosocyanides have specific rotation opposite in sign to that exerted by the corresponding nitrosochlorides.

Several other questions remain for further investigation, among them an inquiry as to the nature of the union between the two semimolecules of the nitrosochlorides.

The substitution or withdrawal of the chlorine certainly renders the bisnitroso-linking unstable, but it does not appear to follow in all cases that the presence of the chlorine prevents the assumption of the oxime constitution by the nitroso-group, or that on the removal of the chlorine the derivative is necessarily unimolecular.

Experimental.

Preparation of the Isomeric Limonene Nitrosocyanides.

The *d*-limonene employed in these experiments was the fraction of sweet orange oil boiling at 174—176°, having sp. gr. 0·8664 at 15°, and α_D 100°22·5′ in a 1-dcm. tube, whence $[\alpha]_D$ 115·2°; a solution in chloroform gave $[\alpha]_D$ 119·9°. The *l*-limonene obtained from Messrs. Schimmel distilled at 172—176°, had a sp. gr. 0·8658 at 19°, and gave α_D − 97°27′ in a 1-dcm. tube, whence $[\alpha]_D$ − 112·3°.

These hydrocarbons were converted into the nitrosochlorides by Wallach's process (*Annalen*, 1889, **252**, 108), but in quantities twenty times those mentioned, addition of hydrochloric acid being temporarily

discontinued when the precipitation of the nitrosochloride induces a rapid rise of temperature; at the conclusion of the operation, 100 c.c. of alcohol were added, 75 grams of the isomeric products being thus obtained from every 100 c.c. of hydrocarbon. In order to separate the α- and β-nitrosochlorides, 150 grams of the mixture were added to 450 grams of chloroform, which dissolved the major portion, forming a deep blue liquid, the undissolved portion consisting of crude β-nitrosochloride, which was reprecipitated by methyl alcohol from the solution in 10 parts of chloroform, and finally washed with dry ether.

The bulk of both the α- and β-compounds was, however, obtained from the first solution in chloroform, from which, by adding methyl alcohol, the β-nitrosochloride was precipitated, together with the greater quantity of the α-compound, which is finally purified by dissolution in ether and precipitation with methyl alcohol, 68—70 grams of the α-nitrosochloride and 40—42 grams of the β-nitrosochloride being obtained from 150 grams of the crude mixture. Owing to the large production of a yellow oil, which arises from the action of potassium cyanide on the limonene nitrosochlorides, it has been necessary to modify the method of preparation previously indicated (Trans., 1904, **85**, 931). The following process gives the best results.

Twenty grams of the pure α- or β-nitrosochloride were ground to a fine powder with 12 grams of potassium cyanide; alcohol was gradually added up to 120 c.c., the mixture being kept at 25—30°. Potassium chloride was soon deposited, whilst the liquid assumed a pale yellow colour, which deepened as the reaction proceeded, the nitrosochloride gradually disappearing; the α-nitrosochloride was completely changed in about 5 days, the β-compound requiring about 15 days, but these rates are influenced very considerably by variation in temperature. Pouring the alcoholic solution into water precipitated a colourless oil, which soon became semi-solid and weighed 18 grams; washing with light petroleum and crystallisation from the same solvent furnished two optically active nitrosocyanides, of which the preponderating modification formed thick prisms (7 grams) melting at 90—91°, the remainder (0·5 gram) crystallising in slender needles and melting at 140—141°. The less fusible isomeride is also deposited in part from the light petroleum washings, and purified by solution in chloroform and precipitation with petroleum. When the reaction is carried out above 30°, this isomeride is not readily produced. Attempts have been made to increase the yield of the nitrosocyanides by dissolving the α-nitrosochloride in ether, mixtures of alcohol with ether and of water with ether, instead of alcohol, and no better results were obtained by substituting different metallic cyanides for potassium cyanide. The α- and β-nitrosochlorides both give rise to approximately

30—35 per cent. of α-nitrosocyanide, accompanied by 2—3 per cent. of the β-modification, the remaining 60 per cent. being transformed into an oil the composition of which has not been determined.

d- *and* l-*Limonene α-Nitrosocyanides,* $C_{10}H_{15}{<}^{NOH}_{CN}$.

The dextro-compound has been already described (Trans., 1904, **85**, 932). Both the *d*- and *l*-α-nitrosocyanides crystallise from dilute alcohol in long, colourless, transparent, four-sided prisms, also from light petroleum in flattened prisms, readily soluble in ether, chloroform, and hot petroleum, sparingly so in cold petroleum, and insoluble in water. They melt at 90—91° without decomposition, fusing again at the same temperature. The compounds are soluble in dilute aqueous alkali, and are reprecipitated by the addition of dilute acid; a solution of bromine in chloroform is readily decolorised, and halogen acids are fixed by the cyanides. When crushed, the α-nitrosocyanides become very electrified, clinging tenaciously to the vessel. Towards hot aqueous or alcoholic potash they behave like normal nitriles, being readily hydrolysed to the corresponding amide or acid with evolution of ammonia.

The α-nitrosocyanides gradually dissolve with evolution of heat in concentrated sulphuric acid, producing a yellow, and finally a deep red, colour; on pouring the solution into water, the liquid remains clear, but on neutralising with ammonia a white, gelatinous precipitate is formed, which has not been further investigated. When heated with dilute acids, the nitrosocyanides readily yield hydroxylamine together with dark coloured, uncrystallisable products.

The α-nitrosocyanides are optically active, the sign of the rotation being the same as that of the nitrosochlorides from which they are derived.

0·5692 gram of the dextro-α-nitrosocyanide, dissolved and made up to 25 c.c. with chloroform, gave a mean rotation of +6°57·3′ at 18·5° in a 2-dcm. tube, whence $[\alpha]_D$ +152·7°.

0·5524 gram of the lævo-α-nitrosocyanide in a similar way at 19° gave a mean rotation of −6°43·5′, whence $[\alpha]_D$ −152·2°.

0·1084 [*d*-] gave 14·2 c.c. nitrogen at 19·5° and 760 mm. N = 15·02.
0·1526 [*l*-] „ 19·6 c.c. „ 16° „ 760 mm. N = 14·98.
$C_{11}H_{16}ON_2$ requires N = 14·58 per cent.

Molecular weight determinations by the cryoscopic method gave :

	Weight of benzene.	Weight of substance.	Depression Δ.	Molecular weight.
Lævo-	19·29	0·0780	0·110	180·1
,, ...	19·29	0·1812	0·235	195·9
Dextro-	20·68	0·0466	0·080	138·0
,, ...	20·68	0·1096	0·170	152·6
,, ...	20·68	0·1784	0·250	168·7
,, ...	19·8	0·2204	0·300	181·8
,, ...	19·8	0·3318	0·420	195·4

$C_{11}H_{16}ON_2$ requires 192.

0·0991 gram in 19·3 grams of naphthalene gave Δ = 0·1875° for the dextrorotatory compound, whence M.W. = 191·6.

In their unimolecular character, therefore, the *d*- and *l*-α-nitrosocyanides resemble the limonene nitrolamines.

The *benzoyl* derivatives, $CN\cdot C_{10}H_{15}⁚NO\cdot CO\cdot C_6H_5$:

The *d*- and *l*-α-nitrosocyanides readily yield benzoyl derivatives by the Schotten-Baumann method; these crystallise from dilute alcohol in thin leaves or plates melting at 108°. They are readily soluble in chloroform and ether, and may also be crystallised from petroleum.

0·5092 gram of the *l*-benzoyl derivative, when dissolved and made up to 25 c.c. with chloroform, gave a mean rotation of − 5°11′ at 15° in a 2-dcm. tube, whence $[\alpha]_D$ − 127·2°.

0·5478 gram of the *d*-benzoyl derivative, treated in the same manner at 19°, gave a mean rotation of + 5°32·25′, whence $[\alpha]_D$ + 126·3°.

0·1496 [*d*-] gave 12·4 c.c. nitrogen at 20·5° and 767 mm. N = 9·55.
0·1728 [*l*-] ,, 14·6 c.c. ,, 18° ,, 760 mm. N = 9·76.
$C_{18}H_{20}O_2N_2$ requires N = 9·46 per cent.

The *methyl ether*, $CN\cdot C_{10}H_{15}⁚NO\cdot CH_3$, of the *d*-α-nitrosocyanide is a viscous oil, which is readily prepared by the action of methyl iodide and caustic potash in methyl alcohol, also by the use of silver oxide.

The *ethyl ether*, $CN\cdot C_{10}H_{15}⁚NO\cdot C_2H_5$, prepared in the same way, is also an oil. On passing dry hydrogen chloride through a solution of this ether in methyl alcohol, the characteristic hydrochloride is precipitated; it crystallises from dilute alcohol in large, hexagonal plates which melt at 44°. This compound was produced with the object of comparing it with the hydrochloride which is formed by the yellow oil obtained in the preparation of the nitrosocyanides, it being possible that ether formation takes place during the separation of the two halves of the bimolecular nitrosochloride. The hydrochloride of the yellow oil, however, melts at about 165° and does not resemble the foregoing substance.

The *hydrochloride* of *d*-α-nitrosocyanide, $CN\cdot C_{10}H_{16}(NOH)Cl$, is

readily obtained by adding the elements of hydrogen chloride; it crystallises from dilute alcohol in thin, transparent plates which melt at 56°.

d- *and* l-*Limonene β-Nitrosocyanides,* $C_{10}H_{15}{<}^{NOH}_{CN}$.

The preparation of these compounds has been described. They crystallise in fine, woolly needles from chloroform on addition of petroleum, and in somewhat longer needles from dilute alcohol.

In order to effect a complete separation of the β-nitrosocyanide from the α-compound, the crude mixture is dissolved in a little chloroform and light petroleum added; the β-isomeride, being the less soluble, is precipitated, whilst small quantities of the α-nitrosocyanide with oily matter remain in solution. The melting point gradually rises after each precipitation until it reaches 140—141° with no perceptible decomposition, but distinct softening takes place at 138°. Recrystallisation from hot light petroleum depresses the melting point, probably owing to slight decomposition. The *d*- and *l*-β-nitrosocyanides are less soluble in all ordinary solvents than the corresponding α-nitrosocyanides. They resemble the latter, however, in their solubility in dilute aqueous alkalis, being reprecipitated on addition of dilute mineral acids; if boiled with dilute acids, however, they yield hydroxylamine, but not so readily as the α-nitrosocyanides.

Action of Aqueous Alkali.—Although the quantity of the β-isomeride is small, it has been found that, on treatment with 25 per cent. aqueous potassium hydroxide, like the α-nitrosocyanide, it readily evolves ammonia, and most probably the corresponding acid is formed. The acid, however, has not been isolated, but only the product of its decomposition, namely, the oxime of dihydrocarvone, which melts at 88·5°, and is identical with that obtained by the hydrolysis of the α-nitrosocyanide.

The limonene β-nitrosocyanides are optically active, but in the opposite sense to the nitrosochlorides from which they are derived.

0·4672 gram of the *d*-β-nitrosocyanide, when dissolved and made up to 25 c.c. with chloroform, gave a mean rotation of $-1°11'$ at 19° in a 2-dcm. tube, whence $[\alpha]_D - 31·6°$.

0·4528 gram of the *l*-β-nitrosocyanide in a similar manner gave a mean rotation of $+1°6·5'$ at 19°, whence $[\alpha]_D + 30·6°$.

0·1246 [*d*-] gave 16·1 c.c. nitrogen at 19·5° and 773 mm. N = 15·07.
0·1020 [*l*-] ,, 13·3 c.c. ,, 19° ,, 762 mm. N = 15·03.
$C_{11}H_{16}ON_2$ requires N = 14·58 per cent.

Determinations of the molecular weight in benzene gave the following results:

	Weight of benzene.	Weight of substance.	Depression Δ.	Molecular weight.
Dextro-	18·94	0·0979	0·115	220·2
,, ...	18·94	0·1911	0·215	229·9
Lævo-	20·68	0·0840	0·095	209·5
,, ...	20·68	0·1542	0·165	221·4

$C_{11}H_{16}ON_2$ requires 192.

The *benzoyl* derivatives, $CN\cdot C_{10}H_{15}\colon NO\cdot CO\cdot C_6H_5$, are readily prepared by the Schotten-Baumann reaction, which crystallises from dilute alcohol in beautiful, long, silky needles melting at 121°, and yielding a somewhat soft, coherent mass when crushed. 0·5042 gram of the *d*-benzoyl dissolved and made up to 25 c.c. with chloroform gave a mean rotation of $-4°22'$ at 18° and in a 2-dcm. tube, whence $[\alpha]_D -108·2°$.

0·5324 gram of the *l*-benzoyl, in a similar manner, gave a mean rotation of $+4°38'$ at 18·15°, whence $[\alpha]_D +108·7°$. The sign of rotation is the same as that of the corresponding nitrosocyanides.

0·1635 [*d*-] gave 14·1 c.c. nitrogen at 19° and 765 mm. N = 9·97.
0·1618 [*l*-] „ 13·8 c.c. „ 15° ,, 743 mm. N = 9·76.
$C_{18}H_{20}O_2N_2$ requires N = 9·46 per cent.

The d- *and* l-α-*Amides*, $C_{10}H_{15}<^{NOH}_{CO\cdot NH_2}$.

Twenty grams of the *d*- or *l*-limonene α-nitrosocyanide were heated on the steam-bath for about 8 days in a reflux apparatus with 25 grams of potassium hydroxide, dissolved in absolute alcohol, when the solution gave no precipitate on acidification with dilute hydrochloric acid. During the process, small quantities of ammonia were evolved, the liquid developing a brown colour, and on adding acetic acid the solution yielded a semi-solid paste which soon became crystalline. The crude product, weighing 17·5 grams, was dissolved in chloroform and precipitated with petroleum, and on repeating this operation several times, the amide became colourless and separated in tufts of slender, bulky needles. It crystallises in somewhat larger needles on adding petroleum to an ethereal solution, and melts at 138° with slight decomposition. Alcohol dissolves it very readily, dilution precipitating it incompletely; it is soluble also in dilute aqueous alkalis and acids. It readily decolorises a solution of bromine in chloroform and unites with halogen hydrides.

The *d*- and *l*-α-amides are optically active in the same sense as the nitrosocyanides and nitrosochlorides from which they are derived.

0·5050 gram of the *d*-α-amide, dissolved in chloroform and made

up to 25 c.c., gave a mean rotation of $+7°4'$ at 17° and in a 2-dcm. tube, whence $[\alpha]_D$ $+174·9°$.

0·5242 gram of the *l*-*α*-amide, in a similar manner, gave a mean rotation of $-7°17·8'$ at 19°, whence $[\alpha]_D$ $-174·0°$.

0·1258 [*d*-] gave 14·6 c.c. nitrogen at 24° and 766 mm. N = 13·13.
0·1280 [*l*-] „ 15·0 c.c. „ 15° „ 744 mm. N = 13·43.
$C_{11}H_{18}O_2N_2$ requires N = 13·33 per cent.

The *methyl ether* is a viscous liquid resembling the methyl ether of the *α*-nitrosocyanide.

The *benzoyl* derivatives are prepared by the Schotten-Baumann reaction and crystallise from dilute alcohol in rhombic prisms, which melt sharply at 152° without decomposing. They are optically active, the introduction of the acyl group increasing the rotation strongly.

0·4180 gram of the *d*-benzoyl, dissolved in chloroform and made up to 25 c.c., gave a mean rotation of $+8°5'$ at 19° and in a 2-dcm. tube, whence $[\alpha]_D + 241·7°$.

0·4176 gram of the *l*-benzoyl, in a similar manner, gave a mean rotation of $-8°5'$, whence $[\alpha]_D - 242·0°$.

0·2210 [*d*-] gave 18·2 c.c. nitrogen at 24° and 760 mm. N = 9·23.
0·1667 [*l*-] „ 13·7 c.c. „ 15° „ 745 mm. N = 9·42.
$C_{18}H_{22}O_3N_2$ requires N = 8·91 per cent.

The *hydrochloride* of the *d*-*α*-amide crystallises from dilute alcohol in slender needles and melts at 100—101° without decomposing.

The d- *and l-α-Acids,* $C_{10}H_{15}\lessgtr^{NOH}_{CO_2H}$.

Twenty grams of the *d*- or *l*-*α*-nitrosocyanide were dissolved in 150 c.c. of 25 per cent. aqueous potassium hydroxide and boiled during 24 hours; when the reaction had proceeded several hours, the liquid gave rise to an oil which partly crystallised on allowing the contents of the flask to cool. The oil had a distinct odour of carraway (carvone), or probably of dihydrocarvone. The alkaline liquid, cooled with ice and carefully neutralised with dilute hydrochloric acid, gave 9 grams of the acid in a crystalline and almost colourless condition, together with 2·5 grams of impure acid; the by-products although partly crystalline, have not been fully investigated. The acid was purified by dissolution in a small quantity of alcohol, the solution cooled below 0°, and gradually diluted with water, which precipitated nacreous leaflets melting at 97° and evolving carbon dioxide. Re-

crystallisation was effected as quickly as possible, as the acids decompose in solution and slowly evolve carbon dioxide.

0·1738 [*d*-] gave 10·8 c.c. nitrogen at 17·5° and 751 mm. N = 7·11.
0·1739 [*l*-] „ 10·5 „ „ „ 15° „ 745 mm. N = 6·92.
$C_{11}H_{17}O_3N$ requires N = 6·63 per cent.

The acids rotate the plane of polarisation in the same direction as the hydrocarbons from which they arise.

0·5636 gram of the *d*-acid, dissolved and made up to 25 c.c. with chloroform, gave a mean rotation of +4°38·3′ at 20° and in a 2-dcm. tube, whence $[\alpha]_D$ +102·9°.

0·5732 gram of the *l*-acid gave a mean rotation of −4°46′, whence $[\alpha]_D$ −103·9°.

The rotations of these acids are not constant owing to the decomposition which takes place so readily in solution. In one case, in the course of 45 minutes, the rotation fell from +4°50′ to 4°20′.

The *ammonium* salts were precipitated on passing ammonia into dried ethereal solutions of the acids. Aqueous solutions give precipitates with soluble salts of the heavy metals, but the compounds are not characteristic.

The *silver* salts prepared from aqueous solutions of the ammonium salts and silver nitrate separate in the form of colourless, bulky precipitates. They become brown on exposure to light. For analysis, the substance was washed with alcohol followed by ether, and then dried in a vacuum.

0·3134 [*d*-] gave 0·1058 Ag. Ag = 33·76.
0·1666 [*l*-] „ 0·0560 Ag. Ag = 33·61.
$C_{11}H_{16}O_3NAg$ requires Ag = 33·93 per cent.

The silver salts are soluble in ammonia; the aqueous or ammoniacal solutions rapidly blacken on heating.

The *methyl ester* of the *d*-acid was prepared from the silver salt and methyl iodide diluted with methyl alcohol, absence of diluent involving a vigorous action with blackening and destruction of the substance. The methyl ester melts at 65° and softens at 62°, being difficult to obtain pure owing to admixture with other decomposition products of the acid; it is soluble in dilute aqueous alkali.

0·1983 gave 11·6 c.c. nitrogen at 19° and 758 mm. N = 6·69.
$C_{12}H_{19}O_3N$ requires N = 6·20 per cent.

The readiness with which solutions of the acids lose carbon dioxide in choroform, ether, or alcoholic solution, is remarkable; when dry and pure, they can be preserved in the desiccator, but exposure to the

air involves gradual decomposition. The acids dissolve readily in ammonium carbonate or sodium hydrogen carbonate, but are not soluble in mineral acids or water; at the melting point, a vigorous disengagement of carbon dioxide occurs, and ammonia is also liberated in small quantities. The residue has a strong odour of carraway, and reduces Fehling's solution. It would therefore appear that besides loss of carbon dioxide, a partial elimination of the ⁚NOH group takes place, yielding hydroxylamine and the ketone dihydrocarvone. These facts serve to account for the variety of products obtained on hydrolysing the cyanides.

In order to ascertain the proportion of carbon dioxide lost by the α-nitrosoacid, weighed quantities were heated to 130°.

0·5559 gave 0·1129 CO_2. $CO_2 = 20·31$.
0·5335 ,, 0·1082 CO_2. $CO_2 = 20·28$.
$C_{11}H_{17}O_3N$ requires $CO_2 = 20·85$ per cent. for the loss of 1 molecule of carbon dioxide.

The solid residue was associated with a small proportion of dihydrocarvone, and by crystallisation from dilute alcohol the former was obtained in long needles, melting at 88·5°, Wallach (*Annalen*, 1894, **279**, 381) giving the melting point 88—89° for the oxime of dihydrocarvone. The identity of this substance was established by treating it with hydrogen bromide in glacial acetic acid; on pouring the solution into water, a white, crystalline hydrobromide was obtained melting and decomposing at 109—110°. According to Wallach, the normal oxime gives a hydrobromide melting at 109°, whilst the *iso*oxime does not yield a corresponding derivative (*Annalen*, 1894, **279**, 382).

0·1898 [*d*-] gave 14·5 c.c. nitrogen at 24° and 769 mm. N = 8·67.
0·1547 [*l*-] ,, 11·0 c.c. ,, at 16° ,, 769·5 mm. N = 8·41.
$C_{10}H_{17}ON$ requires N = 8·38 per cent.

The following determinations were made of the rotatory powers of the *d*- and *l*-dihydrocarvoximes:

0·4738 gram of the *d*-oxime, dissolved in chloroform and made up to 25 c.c., gave a mean rotation of +0°21·5′ at 20° and in a 2-dcm. tube, whence $[\alpha]_D$ +9·45°.

0·4068 gram of the *l*-oxime gave a mean rotation of −0°18′, whence $[\alpha]_D$ −9·25°.

The Racemic Compounds.

The racemic α-nitrosocyanide was prepared by mixing 2·5 grams each of the *d*- and *l*-α-nitrosocyanides, dissolved in alcohol; water precipitated an oil, which soon crystallised and melted at 81°. The

product dissolves less readily in hot petroleum, and crystallises in small, hard, ill-defined prisms. As would be anticipated from the melting point, the racemic compound is more soluble in common media than the active compounds. Its solution is optically inactive.

0·1442 gave 18·6 c.c. nitrogen at 16° and 746·5 mm. N = 14·75.
$C_{11}H_{16}ON_2$ requires N = 14·58 per cent.

The *benzoyl* derivative crystallises from dilute alcohol in prisms which melt at 96°; it is more soluble than its active components, which melt at 108°.

0·1532 gave 13·4 c.c. nitrogen at 17° and 747·6 mm. N = 9·98.
$C_{18}H_{20}O_2N_2$ requires N = 9·46 per cent.

The racemic *β-nitrosocyanide,* prepared from 1 gram each of the active compounds dissolved in a little alcohol, crystallises in slender needles on dilution, and melts at 159—160° without decomposing. It is less soluble than the active compounds and is optically inactive.

0·1344 gave 17·2 c.c. nitrogen at 17° and 762·5 mm. N = 14·89.
$C_{11}H_{16}ON_2$ requires N = 14·58 per cent.

The *benzoyl* derivative crystallises from dilute alcohol in long, colourless needles with silky lustre and melts at 98°, softening at 96°.

0·1544 gave 13·0 c.c. nitrogen at 18° and 764 mm. N = 9·77.
$C_{18}H_{20}O_2N_2$ requires N = 9·46 per cent.

The racemic *α-amide,* prepared from solutions in chloroform of 2 grams of each of the *d-* and *l*-amides, separates quickly, whilst light petroleum precipitates it as a fine, crystalline powder. It crystallises from alcohol on addition of water in prisms or prismatic needles melting at 155° with slight evolution of gas.

The solution in chloroform was optically inactive.

0·1402 gave 16·2 c.c. nitrogen at 18° and 764 mm. N = 13·43.
$C_{11}H_{18}O_2N_2$ requires N = 13·33 per cent.

The active compounds are extremely soluble in alcohol and are not readily precipitated by addition of water.

The *benzoyl* derivative crystallises from dilute alcohol in hard prisms which melt at 150° without decomposition. The active compounds melt at 152°.

0·1747 gave 13·5 c.c. nitrogen at 16° and 769 mm. N = 9·12.
$C_{18}H_{22}O_3N_2$ requires N = 8·91 per cent.

The racemic *α-acid* separates almost immediately on mixing alcoholic solutions of 3 grams each of the *d-* and *l-α*-acids; it melts at 116° with vigorous evolution of carbon dioxide.

0·2004 gave 11·8 c.c. nitrogen at 18° and 770 mm. N = 6·89.
$C_{11}H_{17}O_3N$ requires N = 6·63 per cent.

The *ammonium* salt separates as a fine, crystalline powder on passing ammonia into the dried ethereal solution of the acid.

The *silver* salt, prepared from an aqueous solution of the ammonium salt and slight excess of silver nitrate, is precipitated in the amorphous condition.

0·3236 gave 0·1088 Ag. Ag = 33·62.
$C_{11}H_{16}O_3NAg$ requires Ag = 33·93 per cent.

The racemic acid resembles the *d*- and *l*-acids in losing carbon dioxide, the racemic oxime of dihydrocarvone being formed; this melts at 115° and crystallises from dilute alcohol in prismatic needles. Wallach (*Annalen*, 1893, **275**, 117) gives 115—116° for the melting point of this oxime.

0·1170 gave 8·7 c.c. nitrogen at 17° and 763 mm. N = 8·66.
$C_{10}H_{17}ON$ requires N = 8·38 per cent.

The Oily By-products.

The yellow oil, which forms some 50—60 per cent. of the total product when the preparation of the nitrosocyanides is conducted at 25—30°, constitutes almost the sole product at higher temperatures; it decomposes when distilled under reduced pressure, and is only very slightly volatile in steam. Dilute alkalis dissolve it sparingly, but it is insoluble in dilute acids, which eliminate hydroxylamine on heating. A solution of bromine in chloroform is immediately decolorised, from which only oily products could be obtained.

When heated with 25 per cent. aqueous potassium hydroxide, the oil gradually dissolves, much ammonia being liberated, and there separates an oil which slowly deposits carvoxime, and on removing this with ether and acidifying the aqueous liquid with hydrochloric acid a colourless specimen of the acid was obtained, identical with that derived from the α-nitrosocyanide; 30 grams of the original oil yielded 5·3 grams of acid and 4·2 grams of carvoxime.

Ten grams of the yellow oil were next dissolved in methyl alcohol and saturated with dry hydrogen chloride; on adding the solution to crushed ice, a semi-solid was precipitated, and on crystallising this from dilute alcohol a small quantity of a compound which melts and evolves gas at 165° was obtained. It becomes discoloured at about 161°, and the crystals possess a peculiar stickiness, which is not removed by recrystallisation. Analysis showed that the substance contains approximately 10 per cent. of nitrogen and 16 per cent. of chlorine, but

these results do not agree with the requirements of any unimolecular compound likely to arise from the foregoing reaction. Molecular weight determinations by the depression of the freezing point of benzene gave the following results:

Weight of benzene.	Weight of substance.	Depression Δ.	Molecular weight.
20·0	0·0792	0·060	323·4
20·0	0·1670	0·125	327·3

The substance is therefore probably bimolecular.

0·5688 gram of the substance, dissolved and made up to 25 c.c. with chloroform gave a mean rotation of $+9^{\circ}\cdot52\cdot6'$ at 19° and in a 2-dcm. tube, whence $[\alpha]_D$ +217°.

The corresponding lævo-compound has not yet been prepared.

The investigation of these compounds, and of the oils obtained from the α- and β-nitrosochlorides will be continued.

I desire to express my indebtedness to Professor Tilden for the valuable advice which I have received from him during the progress of this work.

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LIII.—*The Action of Acetylene on Aqueous and Hydrochloric Acid Solutions of Mercuric Chloride.*

John Samuel Strafford Brame.

The recent publication of papers by Bilz and Mumm (*Ber.*, 1905, **37**, 4417) and by Karl Hofmann (*loc. cit.*, p. 4459) on the production of trichloromercuriacetaldehyde makes it desirable that the author should record experiments on the action of acetylene with mercuric chloride in aqueous solution and in solutions containing hydrochloric acid on which he has been engaged for the last four years.

Aqueous Solutions.

Several constitutions have been suggested by different observers for the white precipitate obtained when acetylene is passed into aqueous solutions of mercuric chloride, but Bilz and Mumm, and also Hofmann, seem to have settled fairly conclusively that it is trichloromercuriacetaldehyde, $C(HgCl)_3\cdot CHO$, and analyses made by the author some

three or four years ago are in fair agreement with such a constitution.

Hofmann regards the action as proceeding through two stages, first the formation of $C_2Hg_3Cl_4$ (*Ber.*, 1899, **32**, 810), and then the hydrolysis of this compound to yield the foregoing aldehyde derivative. He ascribes the high analytical results obtained for chlorine by himself and other observers to small amounts of the former substance which remain undecomposed. It does not appear to have been noted, however, that accompanying the trichloromercuriacetaldehyde, there are almost always small amounts of another substance, Cl·CH⁚CH·HgCl, first described by Biginelli (*Ann. Farm. Chim.*, 1898, 16), to which further reference is made, and that the presence of this substance increases the percentage of chlorine present and lowers the percentage of mercury. This acetylene–mercuric chloride is easily removed by two or three extractions with alcohol in a reflux apparatus. Even after its complete removal, however, analyses made by the author invariably gave too high values for chlorine, and too low values for mercury.

It must, indeed, be pointed out that whilst there is close agreement between the analytical results for this substance made by different observers, there is a considerable difference between these results and the values calculated for $C(HgCl)_3$·CHO, and for the purpose of comparison the details are summarised below, so far as they are available, together with the values calculated from various suggested formulæ. The numbers in brackets give the number of experiments from which the mean values were obtained.

	Analytical values.				Calculated values.			
	Keiser.	Bilz and Mumm.	Hofmann.	Brame.	Kutcheroff.	Keiser (*Amer. Chem. J.*, 1893, **15**, 535).	Peratoner (*Gazzetta*, 1894, **24**, [ii], 36).	Hofmann—Bilz and Mumm.
Hg ...	79·34 (3)	79·24 (2)	80·08	79·27 (3)	79·33	79·38	80·72	80·28
Cl......	14·56 (2)	14·69	14·82	14·72 (6)	14·06	14·08	14·30	14·23
C	—	3·28 (5)	—	3·10	3·17	4·76	1·61	3·21
H......	—	0·30 (3)	—	0·28	0·26	0·19	0·13	0·13

The values for Kutcheroff's formula are really deduced from the constitution ascribed by him to the corresponding allylene mercury compound, $3HgCl_2,3HgO,(C_2H_2)_2$ (*J. Russ. Chem. Soc.*, 1882, **14**,

326), but which Bilz and Mumm state to be trichloromercuriacetone, $CH_3{\cdot}CO{\cdot}C(HgCl)_3$.

The agreement between the analytical results and those calculated for such a constitution is really better than for the compound $C(HgCl)_3{\cdot}CHO$, except that the chlorine is abnormally high, but one would expect, if a formula based on Kutcheroff's allylene compound were correct, that acetylene would be liberated on heating, which is not actually the case. The formula indicated by Hofmann and by Bilz and Mumm is, therefore, most likely correct, but the author hopes to conduct further experiments in order to ascertain whether the analytical methods are at fault or whether the substance operated on is impure.

Hofmann (*loc. cit.*) states that there is no precipitation in the presence of a large excess of sodium chloride, but at least with a ratio of five molecules of salt to one molecule of mercuric chloride the precipitate is slowly formed.

Hydrochloric Acid Solutions.

A solution of mercuric chloride in dilute hydrochloric acid has been recommended by Bergé and Reychler (*Bull. Soc. chim.*, 1897, **17**, 218) as a purifying agent for acetylene, on which they say it has no action. This agent is certainly of considerable value as a test for impurities in that gas, and having frequently employed it for that purpose, the author observed after some hours the formation of fine, needle-shaped crystals, the gas washing-bottle being still full of acetylene. On referring to the literature of the subject, it was found that Biginelli (*Ann. Farm. Chim.*, 1898, 16) had obtained a similar result, and from estimations of mercury and chlorine only, ascribed to it the formula $CHCl{:}CH{\cdot}HgCl$. The author has prepared several pure specimens and complete analyses are in good agreement with this.

In addition to the properties already described, it may be mentioned that the material produces intense irritation of the skin, especially on the face, and when dissolved in water, in which it is slightly soluble, gives only a white precipitate with potassium iodide, which serves as a valuable test for the freedom of the product from mercuric chloride. This white precipitate soon undergoes a change to a yellow substance, but all attempts to collect some and purify it for examination have so far failed. When perfectly pure, the dry substance is not darkened by ammonia. On heating, acetylene is given off, this being a point of some importance as supporting the constitution suggested by Biginelli.

Action of Water and Sodium Hydroxide on CHCl:CH·HgCl.

On boiling with water, a white powder is produced to which Biginelli ascribed the formula CH_2:CH·HgCl. The author of this paper has prepared several specimens, but the analytical results do not agree in the slightest with such a constitution.

The crystalline acetylene-mercuric chloride was heated in the water-bath with fresh portions of water until no turbidity was obtained on adding silver nitrate, and only a straw colour on passing sulphuretted hydrogen through the wash water. Acetaldehyde is always produced, the solution becoming strongly acid.

The following results were obtained, the mercury and chlorine being determined at the same time by the lime method:—

					Hg.	Cl.
I.	1·2823	gave	1·0463 Hg	=	81·57	—
	,,	,,	0 7360 AgCl	=	—	14·19
II.	0·6864	,,	0·5576 Hg	=	81·24	—
	,,	,,	0·4040 AgCl	=	—	14·55
III.	0·7964	,,	0·6416 Hg	=	80·56	—
	,,	,,	0·4652 AgCl	=	—	14·44
IV.	0·9728	,,	0·7895 Hg	=	81·15	—
	,,	,,	0·5712 AgCl	=	—	14·52
V.	1·1616	,,	0·9469 Hg	=	81·52	—
	,,	,,	0·6844 AgCl	=	—	14·57

Combustions.

					C.	H.
2·2910	gave	0·2344 CO_2;	0·0383 H_2O	=	2·79	0·18
2·1526	,,	0·1616 ,,	0·0241 ,,	=	2·05	0·13
2·5425	,,	0·1868 ,,	0·0254 ,,	=	2·00	0·11

Mean values from above = Hg = 81·21; Cl = 14·45; C = 2·28; H = 0·13 per cent.

4HgCl,C_2HO requires Hg = 81·40; Cl = 14·43; C = 2·44; H = 0·10 per cent.

Biginelli's C_2H_3·HgCl requires Hg = 76·21; Cl = 13·51; C = 9·14; H = 1·14 per cent.

There can be little doubt but that the substance is a mixture of trichloromercuriacetaldehyde and mercurous chloride in almost molecular proportions, and its behaviour fully bears out this view. On warming with dilute hydrochloric acid in a water-bath, the substance nearly all dissolves with the production of acetaldehyde and mercuric chloride, but a small amount of mercurous chloride remains, which by

the action of the acetaldehyde soon becomes reduced to metallic mercury.

The presence of the mercurous chloride in the first place is easily accounted for by the action of the acetaldehyde liberated on the mercuric chloride also set free on hydrolysis, and must be regarded as accidental, the true product being exactly the same as is produced on passing acetylene into aqueous mercuric chloride.

The crystalline acetylene–mercuric chloride is soluble in alkalis, and on heating the solution a greyish-white precipitate is deposited, which, when examined under the microscope, generally shows globules of finely divided mercury. Biginelli (*loc. cit.*), from apparently one mercury estimation, assumed that this substance was a di-acetylide, $(C_2H_2)_2,HgO$.

In order to obtain the substance as free as possible from metallic mercury, a large number of experiments were made by the author, and ultimately it was found that the best results were obtained by shaking the mercuric compound in small quantities at a time with sodium hydroxide solution and filtering through glass wool into a large volume of hot water. After washing by decantation with hot water until the washings were free from chlorine, the material was dried on porous plates and then under diminished pressure over sulphuric acid, finally being kept for several weeks in a vacuum over phosphoric oxide. The substance ultimately lost weight very slowly, and the drying is therefore a lengthy process. Heating is inadmissible, for the thoroughly dried material steadily loses weight in the water-oven and changes in character.

The dry substance is bluish-white, free from chlorine, and very explosive either when heated or rubbed in a mortar. With the exception of any free mercury, the material is soluble in dilute hydrochloric acid, and this gives a fairly good method of ascertaining the purity, samples which showed more than a trace of the latter being rejected.

Much trouble was experienced in making satisfactory estimations of the mercury, neither the action of sulphuretted hydrogen in hydrochloric acid solution nor the direct decomposition of the substance by ammonium sulphide giving satisfactory results. Ultimately, the method of Frankland and Duppa (*J. Chem. Soc.*, 1863, **15**, 417) was adopted. The material was carefully mixed with copper oxide in the combustion tube, the latter drawn out about five inches from the exit end, a boat containing phosphoric oxide slipped in, and a tapped calcium chloride tube attached, the whole apparatus being exhausted to a few millimetres pressure, dry air was admitted, and the tube again exhausted daily for some three weeks. To make quite sure that no mercury vapour passed into the sulphuric acid tube during combustion, a few strips of silver foil were inserted in the small side tube.

The analytical data for the three purest specimens are:—

				Hg.	C.	H.
1·0570 gave	0·9162 Hg;	0·3824 CO_2;	0·0360 H_2O.	86·68	9·86	0·38.
1·1040 „	0·9694 Hg;	0·3904 CO_2;	0·0334 H_2O.	87·25	9·64	0·34.
1·0609 „	—	; 0·3826 CO_2;	0·0239 H_2O.	—	9·83	0·25.
			Mean	86·96	9·77	0·32.

Biginelli's $(C_2H_2)_2HgO$ requires Hg, 74·63; C, 17·91; H, 1·49 per cent.
Travers and Plimpton's $3C_2Hg,H_2O$ requires Hg, 86·96; C, 10·43; H, 0·29 per cent.

It will be seen that the compound gives results agreeing very closely with those required for the acetylide described by Travers and Plimpton (Trans., 1894, **65**, 264), except that the carbon is unaccountably low. Moreover, the substance generally agrees in its properties with the other acetylide, and there is every reason to believe that it is identical with this, although perhaps it is not quite pure.

Keiser (*Amer. Chem. J.*, 1893, **15**, 535) describes an anhydrous acetylide, HgC_2, but Travers and Plimpton (*loc. cit.*) were unable to obtain the substance free from water, and as Keiser's work seems to be unconfirmed the author is at present engaged in attempting to prepare an anhydrous acetylide.

Conclusions.

There seems good reason for believing that the first action of acetylene on either aqueous or dilute acid solutions of mercuric chloride is the formation of the compound Cl·HC⁚C·HgCl by direct addition together with acetaldehyde. This additive compound has been shown to undergo decomposition with water, producing acetaldehyde, mercuric chloride, free hydrochloric acid, and some trichloromercuriacetaldehyde. The latter is decomposed by hydrochloric acid, and in the presence of much acid is therefore not isolated. It remains to be proved whether it is an intermediate substance concerned in the production of acetaldehyde, or whether it is a secondary substance derived from the aldehyde.

It is hoped to study the exact mechanism of the reaction further, for it should throw considerable light on the remarkable influence exerted by mercury salts in bringing about the formation of acetaldehyde from acetylene in the presence of water.

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LIV.—*The Action of Carbon Monoxide on Ammonia.*

By Herbert Jackson and Dudley Northall-Laurie.

When a mixture of dry carbon monoxide and ammonia is heated in the presence of platinum, subjected to the silent electrical discharge, to electric sparking, or treated with the high frequency current, combination occurs, and ammonium cyanate is formed as the main product, which, as the temperature rises, is rapidly converted into carbamide.

Kuhlmann (*Annalen*, 1841, **38**, 62), who passed carbon monoxide and ammonia over heated platinum black and obtained ammonium cyanide, gave the reaction as

$$CO + 2NH_3 = NH_4{\cdot}CN + H_2O,$$

and this equation has generally been accepted as representing the behaviour of the two gases when heated together.

We find that the amount of cyanide formed is small, and that the main reaction is not the one indicated above.

After various trials with different forms of apparatus, it was found that a spiral of platinum wire sealed inside a glass bulb, and heated by the electric current, gave the best results, and enabled us to study the reaction at different stages. The following observations were made.

On heating the spiral, a white cloud was immediately formed, which condensed on the upper part of the bulb. As the heat increased, this condensation melted, and crystals appeared lower down in the bulb. Water was formed as the experiment proceeded, and by long continued action a white solid was obtained on the cooler parts of the bulb. After many hours, small amounts of a brown substance were also obtained.

Analyses of the various products gave the following results. The first white solid was found to be ammonium cyanate. The crystals formed gave the reactions and the percentage numbers for carbamide. The white solid from the cooler parts of the bulb was found to be ammonium carbonate, and was proved to be due to the action of water on a portion of the carbamide. The brown solid could not be obtained in sufficient quantity for complete analysis, but gave the reactions of polymerised cyanogen compounds. In the cooler tubes leading from the bulb, more ammonium carbonate was found mixed with the small amount of ammonium cyanide formed. This amount was always found to be very small, and bore no relation to the amount of carbamide formed, which in one experiment weighed a little over ten grams. Roughly, this quantity of

carbamide required about eight litres of carbon monoxide, this gas being always in excess under the conditions of the experiment. No biuret was formed, although the temperature was high enough in parts of the bulb to allow of its formation. The presence of free ammonia would account for this, for on passing this gas over heated carbamide the latter remains unaltered, although the temperature may be well above that required for the production of biuret.

The gases which passed from the apparatus were frequently analysed, and found to consist of carbon monoxide, hydrogen, methane, and nitrogen. Numerical results for these gases were obtained in several cases, but as the proportions of the different constituents varied with the conditions of the experiment, it is not necessary to give the results in detail, as they would be little more than statistical and misleading without elaborate description of all the conditions of each experiment.

Referring to the various methods of bringing about the action between carbon monoxide and ammonia, it may be generally stated that the heated spiral of platinum wire, heated platinised asbestos, and the ordinary spark from an induction coil gave the best yields of ammonium cyanate and carbamide, whilst the silent discharge and high frequency current favoured the production of complicated cyanogen compounds. We intend to study these effects more fully in experiments on the polymerising effect of high frequency currents.

There are many possible ways of representing the formation of carbamide in the circumstances described, but so far as we can gather from synthetical and analytical results and from the amounts of hydrogen formed, the simplest view appears to be the formation of ammonium cyanate, thus:

$$CO + 2NH_3 = OCN{\cdot}NH_4 + H_2,$$

and its subsequent change into carbamide. The interaction of free hydrogen with carbon monoxide furnishes the water and the methane. A careful study of the reaction made by working on a large scale and stopping as soon as the first cloud was well formed showed that the first and immediate change was the production of ammonium cyanate and hydrogen, and that the other substances obtained were the result of subsequent reactions, which became the more complicated the longer the time during which the action was allowed to continue.

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LV.—*The Condensation of Phenylglycinoacetic Esters in Presence of Sodium Alkyloxides.*

By ALFRED THEOPHILUS DE MOUILPIED.

THE reaction taking place between ethyl phenylglycine and sodium alkyloxides has been investigated by Vorländer and the author (*Ber.*, 1901, **33**, 2467). Condensation resulted, but the products varied with the solvent employed. In alcoholic solution, the anhydride $\alpha\gamma$-diphenyldiacipiperazine was formed, whilst in benzene solution an isomeride was obtained having very different properties. This was found to be anilino-*N*-phenylhydroxypyrroline, analogous to the compounds obtained by Rügheimer with the esters of hippuric acid. This condensation to ring compounds by the loss of two molecules of alcohol led me, at the suggestion of Professor Vorländer, to examine the reaction taking place between sodium alkyloxides and a number of substituted alkyl phenylglycinoacetates, both when alone and in presence of a third substance such as benzaldehyde or ethyl oxalate.

This investigation seemed to be of interest, because the use of sodium ethoxide in the synthesis of ring compounds by a reaction analogous to the formation of ethyl acetoacetate has been comparatively limited. The condensations undergone by succinic and malonic esters are well known and ring formations of this type have also been studied by W. Wislicenus (*Annalen*, 1888, **246**, 252) and by Auwers (*Ber.*, 1893, **26**, 364). We owe to W. Dieckmann, who has applied it with great success to the higher members of the group of the fatty dibasic acids, the most important recent development of the method (*Ber.*, 1904, **27**, 965; *Annalen*, 1901, **27**, 317). He found that the formation of penta- and hexa-methylene derivatives took place easily, that the formation of seven-membered rings was far more difficult and that it was impossible to obtain rings containing less than five or more than seven members, results which are in accord with von Baeyer's "strain theory." The method is extended in this work to the esters of dibasic acids containing a nitrogen atom linked to a phenyl group in the place of a methylene group.

The objects in view were:

1. To study the influence of the nitrogen atom.

2. To see whether the unsaturated condition of the nitrogen had a further effect.

Ethyl phenylglycinoacetate may thus be compared with ethyl glutarate, $C_6H_5\cdot\overset{|}{\underset{|}{N}}(CH_2\cdot CO_2\cdot C_2H_5)_2$ with $CH_2(CH_2\cdot CO_2\cdot C_2H_5)_2$, and the nitrogen in the former may be regarded as unsaturated. In this

particular case, experiments showed that condensation could not be induced and that saponification alone takes place.

On the other hand, ethyl phenylglycinopropionate, which is described later, condensed in presence of sodium ethoxide to a phenylhydroxypyrroline derivative, behaving in the same manner as ethyl adipate. Up to this point, therefore, the nitrogen has no special influence beyond the fact that the yields are somewhat inferior to those obtained by Dieckmann.

The reaction next investigated was that found to take place between ethyl phenylglycinoacetate and benzaldehyde in benzene solution and in the presence of the theoretical amount of sodium ethoxide. The product which has the formula $C_{19}H_{19}O_4N$ and the following constitution, $CO<\genfrac{}{}{0pt}{}{O-CHPh}{CH_2\cdot NPh}>CH\cdot CO_2\cdot C_2H_5$, is a lactone, yielding the corresponding acid on saponification. Ethyl *o*-tolylglycinoacetate behaved similarly.

The most interesting results were obtained in consequence of the condensations brought about by sodium alkyloxides between various esters of phenylglycinoacetic acid and oxalic acid.

Ethyl phenylglycinoacetate (1 mol.), ethyl oxalate (1 mol.), and sodium ethoxide (2 mols.), when heated, interact energetically and completely, and, on acidifying the sodium salt obtained, a well-defined crystalline product separated which melted at 137°.

It was thought at first that this compound was a pentamethylene derivative obtained in the following manner:

$$C_6H_5N<\genfrac{}{}{0pt}{}{CH\cdot(CO_2Et)\,H\;\;EtO\,OC}{CH\cdot(CO_2Et)\,H\;\;EtO\,OC} \longrightarrow C_6H_5\cdot N<\genfrac{}{}{0pt}{}{CH(CO_2Et)\cdot CO}{CH(CO_2Et)\cdot CO}.$$

Analysis led to the formula $C_{16}H_{17}O_6N$, which accords with this supposition, but the properties of this substance were found to differ greatly from those of the compound obtained by Dieckmann on condensing ethyl glutarate and oxalate in presence of sodium ethoxide. It was expected that on saponification with dilute acids a ketonic hydrolysis would take place, yielding a new type of ortho-diketonic five-membered ring with the group $N\cdot C_6H_5$ replacing one of the methylenes of the pentamethylene nucleus. But saponification could not be brought about, either by acids or alkalis, whether on heating or after prolonged digestion at the ordinary temperature. This seemed to preclude the presence of carboxyl groups in the manner suggested and also the foregoing formation.

No action took place between the compound and hydroxylamine or phenylhydrazine; in fact, it crystallised unchanged from the latter. Further, it is insoluble in aqueous sodium carbonate in the cold, but dissolves in sodium hydroxide with the formation of a yellow salt.

The alcoholic solution gives a reddish-blue coloration with ferric chloride, and the compound is precipitated from an ethereal solution by means of dry ammonia. Finally, it reacts with phenylcarbimide. These properties indicate the enolic character of the substance, and the existence of a yellow sodium salt suggested the possibility of a quinonoid structure arising in the following way :

$$C_6H_5\cdot N\Big<{CH_2\cdot CO_2Et \atop CH\ H\ \cdot CO_2Et} + {CO_2Et \atop CO\,OEt} \longrightarrow$$

$$C_6H_5\cdot N\Big<{CH_2 \text{———} CO\,OEt \atop C\cdot(CO_2Et)\colon C(O\,H)\ \cdot CO_2Et} \longrightarrow CH_2\Big<{CO\cdot O\cdot C\cdot CO_2Et \atop NPh-C\cdot CO_2Et} \longrightarrow$$

$$CH\Big<{C(OH)\cdot O\cdot C\cdot CO_2Et \atop NPh\text{——}C\cdot CO_2Et}.$$

This formula explains several of the properties of this new substance, but does not account for the fact that it does not undergo saponification. A substance of this type described by Guthzeit and Dressel (*Ber.*, 1893, **26**, 2795) was readily saponified.

Ethyl phenylglycinoacetate still possesses some basic properties and dissolves in hydrochloric acid, but this compound is insoluble.

The manner in which the molecules of alcohol are split off was next investigated. If both the –OR groups come from the ethyl oxalate, as they do in the Dieckmann condensations, then it is immaterial whether methyl or ethyl oxalate be used; the product would be the same in both cases :

$$C_6H_5N\Big<{CH\cdot(CO_2Et)\,H \atop CH\cdot(CO_2Et)\,H} + {RO\,OC \atop RO\,OC} \longrightarrow C_6H_5N\Big<{CH(CO_2Et)\cdot CO \atop CH(CO_2Et)\cdot CO}.$$

But on condensing ethyl phenylglycinoacetate with methyl oxalate in presence of sodium ethoxide, a substance was obtained melting at 146—147°.

The third factor was then altered, and it was found that the final result depended on whether sodium methoxide or ethoxide were used. Methyl phenylglycinoacetate was then prepared, and all the possible condensations were carried out with the following results :

Phenylglycinoacetic esters.	Oxalic esters.	Sodium alkyloxides.	Melting point of product.
Ethyl	Ethyl	Ethoxide	137°
Ethyl	Methyl	Ethoxide	146—147
Ethyl	Ethyl	Methoxide	175
Ethyl	Methyl	Methoxide	188
Methyl	Ethyl	Methoxide	188
Methyl	Ethyl	Ethoxide	147
Methyl	Methyl	Ethoxide	159
Methyl	Methyl	Methoxide	195

The influence of the introduction of methyl groups on the melting point is clearly shown, and it is of interest to note that the first condensation takes place far more readily than the last. The methyl group exerts its maximum effect when introduced as methoxide. Some of these products are identical; using the same alkyloxide, it is immaterial whether methyl phenylglycinoacetate and methyl oxalate or ethyl phenylglycinoacetate and methyl oxalate are employed; the esters are interchangeable.

In the other cases, we are probably dealing with structural isomerides, and it is hoped that further work will establish their constitution.

The compound having the formula $C_{16}H_{17}O_6N$ and melting at 137° has been more specially investigated. A completely satisfactory constitutional formula has not been established, but the results obtained show that these condensations give rise to compounds differing very much from those obtained by Dieckmann, and that this difference must be due to the fact that, in the compounds used by the author, a nitrogen atom linked to a phenyl group takes the place of a methylene group.

Experimental.

Preparation of Phenylglycine.

Several methods of preparation have been described, but the yields are not very satisfactory. Michelson and Lippmann (*Compt. rend.*, 1865, **61**, 739), Schultzen and Nencki (*Ber.*, 1869, **2**, 570), and Schwebel (*Ber.*, 1876, **10**, 2045) caused aniline and chloro- or bromoacetic acid to interact in ethereal solution. Hausdörfer (*Ber.*, 1890, **23**, 1987), who allowed them to react in presence of crystallised sodium acetate and a little water, obtained a yield of 26—30 per cent.

The following method was adopted. A mixture of 95 grams (1 mol.) of chloroacetic acid, 186 grams of aniline (2 mols.), and 500 c.c. of water was heated on the water-bath for $1\frac{1}{2}$ hours, shaking frequently, the hot liquid was poured into a dish, and the crystalline product collected and washed with cold water until free from hydrochloric acid. The yield varied between 105 and 120 grams, that is, between 70 and 80 per cent. When prepared in this way, the product contains a small proportion of phenylglycinoacetic acid, which is no disadvantage in view of the next step.

Preparation of Phenylglycinoacetic Acid.

This substance was prepared by the method given by Vorländer and Mumme for *o*-tolylglycinoacetic acid (*Ber.*, 1903, **36**, 1470): 74·5 grams of chloroacetic acid (2 mols.) and 197 grams ($1\frac{3}{4}$ mols.) of soda crystals

are dissolved in 200 c.c. of water; 61 grams (1 mol.) of phenylglycine are then gradually added and the mixture warmed until all has dissolved. The whole is then heated for 2 hours in a boiling water-bath. On adding strong hydrochloric acid to the liquid, a milkiness appears, which disappears on adding an excess. After some time, the phenylglycinoacetic acid crystallises out, and it should be filtered off at once and washed at the pump with cold water until free from hydrochloric acid. The yield is 60—70 per cent.

The proportions were varied at different times, as also the period of heating, and in one case anhydrous sodium carbonate was used, but the foregoing quantities gave the best results.

The acid crystallises from ether in four- or six-sided plates, and from hot water in small pyramids melting at 155—156°.

Preparation of Ethyl Phenylglycinoacetate.

Fifty grams of the acid were heated on the water-bath for 6 hours with quantities of absolute alcohol varying from 100 to 500 grams in presence of 25 grams of concentrated sulphuric acid. The influence of the amount of alcohol used was small provided that at least four times the theoretical amount was used; the yield of ester from 50 grams of acid varied from 30 to 39 grams.

The product was poured into water, the oily ester separated off and dissolved in ether, the ethereal solution washed with dilute aqueous sodium carbonate and dried over anhydrous sodium sulphate. After evaporating off the ether, the ester was distilled under diminished pressure and came over at 195—200° under 17 mm. pressure, the main fraction boiling at 197—198°. The ester is a heavy, colourless oil, the alcoholic solution of which gives no coloration with ferric chloride.

0·2879 gave 0·6640 CO_2 and 0·1880 H_2O. C = 63·04; H = 7·25.
$C_{14}H_{19}O_4N$ requires C = 63·39; H = 7·17 per cent.

In this distillation, a fraction boiling some 30—40° higher than the normal ester was always obtained. This less volatile substance dissolved in sodium carbonate with effervescence and was titrated against standard baryta solution. 0·8528 gram dissolved in absolute alcohol required 5·0 c.c. baryta [1 c.c. = 0 00605 $Ba(OH)_2$], giving a molecular weight of 241, the molecular weight of the acid ester being 237. This non-volatile fraction thus consists of the acid ester of phenylglycinoacetic acid, $CO_2H \cdot CH_2 \cdot NPh \cdot CH_2 \cdot CO_2Et$ (see p. 441).

Methyl phenylglycinoacetate was prepared in a similar manner; it is an almost colourless oil which distils over at 210—211° under 18 mm. pressure; 50 grams of the acid gave 50 grams of the ester, the yield being 52 per cent.

Preparation of o-*Tolylglycinoacetic Acid.*

Tolylglycine was first prepared in the manner described for phenylglycine, from *o*-toluidine and chloroacetic acid. The *o*-tolylglycinoacetic acid was prepared in the same way as the phenyl compound. When recrystallised, it melts at 154—156° with slight decomposition.

Ethyl *o*-tolylglycinoacetate, $C_7H_7N(CH_2{\cdot}CO_2C_2H_5)_2$, was prepared in the manner described for the phenyl ester; it distils at 205—207° under 16 mm. pressure as a viscid, colourless oil, which readily crystallises in beautiful needles melting at 59—60°. The alcoholic solution gives no coloration with ferric chloride.

0·4021 gave 18·0 c.c. nitrogen at 15·5° and 762 mm. N = 5·21.
$C_{15}H_{21}O_4N$ requires N = 5·02 per cent.

Action of sodium ethoxide on ethyl phenylglycinoacetate. (*a*) In benzene solution: 1·2 gram of sodium (1 atom) in the form of wire was placed in dry benzene and rather more than the theoretical amount of alcohol for conversion with ethoxide added. When the sodium had disappeared, 13·25 grams (1 mol.) of ethyl phenylglycinoacetate were added, and after standing 12 hours the whole was heated for $1\frac{1}{2}$ hours. Water was then added, the benzene layer separated off, and the aqueous part was acidified with hydrochloric acid; nothing was precipitated, nor could anything be extracted with ether. Condensation does not take place, and this ester behaves like ethyl glutarate. The benzene portion yielded on evaporation a very small amount of a white substance, which, sparingly soluble in water and alkalis, dissolved readily in alcohol, acetone, or ether. Its alcoholic solution gave a violet coloration with ferric chloride. The compound crystallised from alcohol in needles melting at 170°. On warming the substance with water, the latter acquired an alkaline reaction, and with hydrochloric acid a gummy product was obtained. On attempting to analyse the substance, it was found to leave an ash on combustion, and the percentage of sodium was determined.

0·2522 gave 0·0344 Na_2SO_4. Na = 4·42 per cent.

This sodium salt of high molecular weight has the exceptional property of being soluble in benzene, but dissolving only with difficulty in water.

(*b*) In alcoholic solution, the ester is partially saponified. After heating for half an hour on the water-bath, a sodium salt was precipitated, which was collected, decomposed with hydrochloric acid, and extracted with ether. The product, which crystallised from hot water and melted at 121—122°, is the acid ester,

$$CO_2H{\cdot}CH_2{\cdot}NPh{\cdot}CH_2{\cdot}CO_2Et,$$

already described in the liquid form (see p. 439). This is proved by the fact that on further saponification with 50 per cent. caustic potash it yielded phenylglycinoacetic acid (m. p. 155—156°). Similarly no condensation products were obtained in the case of ethyl *o*-tolylglycinoacetate.

β-Phenylglycinopropionic Acid and its Esters.

Preparation of the Ethyl Ester, $C_6H_5 \cdot N(CH_2 \cdot CO_2Et) \cdot CH_2 \cdot CH_2 \cdot CO_2H$.

A mixture of 10 grams of β-iodopropionic acid (1 mol.) and 18 grams of ethyl phenylglycine (2 mols.) was heated at 90° in the water-bath for $2\frac{1}{2}$ hours; the viscid oily product obtained was treated several times with aqueous sodium carbonate to neutralise the acid ester formed, and the excess of ethyl phenylglycine was extracted with ether. A slight excess of hydrochloric acid was added, and the liquid repeatedly extracted with ether, owing to the solubility of the ester in the acid. After drying and evaporating off the ether, a viscid, faintly yellow oil was obtained, which did not solidify *in vacuo*; the yield was 10—12 grams.

0·2318 gave 10·6 c.c. nitrogen at 16° and 766 mm. N = 5·38.
$C_{13}H_{17}O_4N$ requires 5·58 per cent.

0·5628 required for neutralisation 15·0 c.c. baryta solution.
[1 c.c. = 0·0125 $Ba(OH)_2$]. Equivalent found, 250·6.
$C_{13}H_{17}O_4N$ requires 251.

Preparation of the Isomeric Ester, $C_6H_5 \cdot N(CH_2 \cdot CO_2H) \cdot CH_2 \cdot CH_2 \cdot CO_2Et$.

Ethyl β-iodopropionate was first prepared by heating together for 4 hours, 50 grams of the acid with 200 grams of absolute alcohol containing 1 per cent. of dry hydrogen chloride (Harris, *Ber.*, 1896, 29, 513).

To prepare ethyl β-anilinopropionate, $C_6H_5 \cdot NH \cdot CH_2 \cdot CH_2 \cdot CO_2Et$, 46 grams of ethyl β-iodopropionate (1 mol.) were heated for 20 minutes at 80° with 38 grams (2 mols.) of aniline. Condensation took place with the separation of aniline hydriodide. The mixture was shaken up with water, and the heavy oily product extracted with ether and dried over potassium carbonate. This oil distilled at 175° under 18 mm. pressure, the yield being 30 grams.

Condensation of this Ester with Chloroacetic Acid.—It was found advantageous to work with small quantities. Eight grams (2 mols.) of ethyl β-anilinopropionate were heated in the water-bath with 2 grams (1 mol.) of chloroacetic acid for 3 hours. When cold the solid mass was shaken up with aqueous sodium carbonate, and any unchanged ester extracted with ether. After acidifying with hydrochloric acid, the liquid was repeatedly extracted with ether. The

ethereal solution yielded on evaporation an oil which solidified under diminished pressure. The ester crystallises from aqueous methyl alcohol in rhombic prisms melting at 60—61°. Its alcoholic solution gives no coloration with ferric chloride.

0·2096 gave 10·1 c.c. nitrogen at 16·5° and 766 mm. N = 5·65.
$C_{13}H_{17}O_4N$ requires 5·58 per cent.

0·1517 required for neutralisation 17·4 baryta solution of factor 0·0374. Equivalent found, 238. $C_{13}H_{17}O_4N$ requires 254.

β-Phenylglycinopropionic Acid, $C_6H_5\cdot N(CH_2\cdot CO_2H)\cdot CH_2\cdot CH_2\cdot CO_2H$. —This acid was obtained by the saponification of both the acid esters just described, a reaction which is best brought about by weak alkali at 80°. The potassium salt was obtained in needles which were decomposed by dilute hydrochloric acid, and the solution was extracted with ether. The solid obtained on evaporation was recrystallised from benzene and a little light petroleum, and separated out in white needles melting at 137°. This acid decomposes on heating, and its alcoholic solution gives a reddish-brown coloration with ferric chloride.

0·1560 gave 0·3360 CO_2 and 0·0888 H_2O. C = 58·94 ; H = 6·32.
$C_{11}H_{13}O_4N$ requires C = 59·19. H = 5·82 per cent.
0·0959 required for neutralisation 23·2 c.c. baryta solution.
[1 c.c. = 0·0032 $Ba(OH)_2$]. Equivalent found, 110·5.
$C_{11}H_{13}O_4N$ requires 111·5.

Ethyl β-Phenylglycinopropionate.—The normal ester was prepared from both the acid esters, but it is best obtained from the liquid ester, for in the preparation of the solid ester one-half of the ethyl β-anilinopropionate used is lost. Twenty-five grams of the liquid acid ester were boiled for 6 hours with 250 grams of absolute alcohol and 25 grams of concentrated sulphuric acid. The product was worked up in the usual way and 21 grams of the diethyl ester obtained. This boils at 210—211° under 16 mm. pressure as a colourless, viscid oil.

0·3192 gave 0·7539 CO_2 and 0·2153 H_2O. C = 64·44 ; H = 7·50.
0·3190 ,, 14·0 c.c. nitrogen at 15·5° and 765 mm. N = 5·16.
$C_{15}H_{21}O_4N$ requires C = 64·51 ; H = 7·53 ; N = 5·02 per cent.

Action of Sodium Ethoxide on Ethyl β-Phenylglycinopropionate.— 1·2 grams of sodium wire (1 atom) were placed in 40 c.c. of dry benzene and heated up with rather more than the theoretical amount of absolute alcohol until the metal had disappeared. To this were then added 14 grams (1 mol.) of the ester, and the mixture was boiled for $\frac{1}{2}$ to $\frac{3}{4}$ of an hour in a reflux apparatus. As a rule, the sodium salt which separated was shaken up with water and the benzene

separated from the aqueous layer. The addition of a small amount of ether destroys the emulsion which tends to form. The aqueous part is purified by shaking up with ether, and the last traces of the latter are removed by aspiration. On passing carbon dioxide through the solution, a white substance is precipitated. If acetic acid is used, the precipitate is crystalline. The acidified solution may also be extracted with ether, from which the substance crystallises in needles.

The following method was, however, found to be more satisfactory. The sodium salt is collected and washed with a little alcohol and ether; it is dissolved in water, the filtered solution being then acidified with acetic acid, when the white substance separates in a fairly pure condition. This compound crystallises from aqueous alcohol in small, hexagonal plates and from alcohol in needles; it melts at 69—70°.

0·2012 gave 0·4904 CO_2 and 0·1218 H_2O. C = 66·51; H = 6·70.
0·2338 „ 11·1 c.c. of nitrogen at 16·3° and 768 mm. N = 6·15.
$C_{13}H_{15}O_3N$ requires C = 66·95; H = 6·43; N = 6·01 per cent.
0·1256 in 16·1699 naphthalene gave $\Delta t = 0{\cdot}223°$; M. W. = 242.
$C_{13}H_{15}O_3N$ requires M. W. = 233.

The alcoholic solution gives a dark violet coloration with ferric chloride. The substance dissolves in warm aqueous sodium carbonate, but the sodium salt separates on cooling; it is soluble in hydrochloric acid, but not so readily in caustic alkali. A coloured product is not obtained either by treatment with fuming sulphuric acid or after fusion with caustic potash. With phenylhydrazine, a light yellow product is obtained, melting, after recrystallisation from alcohol, at 160—161°.

Dieckmann found that ethyl adipate condensed in presence of sodium ethoxide to ethyl β-ketopentamethylenecarboxylate by the loss of one molecule of alcohol. This reaction, if on corresponding lines, would yield a substance having the empirical formula $C_{13}H_{15}O_3N$, and both the analysis and the molecular weight found agree with this. The colour reaction with ferric chloride points to an enolic form, as does the existence of salts. This compound has thus in all probability the following constitution:

$$C_6H_5{\cdot}N{<}\begin{matrix}CH_2{\cdot}CH_2\\C(CO_2Et)\end{matrix}{>}C{\cdot}OH \quad \text{or} \quad C_6H_5{\cdot}N{<}\begin{matrix}CH_2{\cdot}C{\cdot}CO_2Et\\ \| \\ CH_2{\cdot}C{\cdot}OH\end{matrix},$$

and is ethyl phenylhydroxypyrrolinecarboxylate.

The saponification of this ester is not easily effected by alkalis. The ester was dissolved in alcohol, an excess of 50 per cent. caustic potash added, and the whole heated on the water-bath. The potassium derivative separates out first, as was shown by the fact that on acidifying it yields the original ester melting at 68°. After heating for two hours, the solid disappeared; the filtered solution was acidified

with dilute sulphuric acid and extracted 12 times with ether. The acid was obtained on evaporation; it crystallised from water and melted at 143—144°.

0·1116 gave 6·1 c.c. of nitrogen at 16·1° and 765 mm. N = 6·42.
$C_{11}H_{11}O_3N$ requires N = 6·83 per cent.

The acid is soluble in cold aqueous sodium carbonate and in acids. The alcoholic solution gives no coloration with ferric chloride. When the acid was heated at 170—180° for 15 minutes, carbon dioxide was eliminated. The oily product was dissolved in alcohol and warmed with a little ferric chloride, when a greenish-blue precipitate was formed. This was collected, washed, and dried, and treated with pure concentrated sulphuric acid; on warming, a violet colour was produced. The amount of substance obtained was so small that further investigation was not possible. This colour reaction is, however, interesting, because it may be compared with the behaviour of phenylmethylpyrazolone (Knorr, *Annalen*, 1887, **238**, 172). On warming an alcoholic solution of ethyl β-phenylglycinopropionate with sodium ethoxide, the ester is partially saponified, and the solid ester, $C_6H_5·N(CH_2·CO_2H)·CH_2·CH_2·CO_2Et$ (m. p. 60—61°), is obtained.

Condensation of Ethyl Phenylglycinoacetate with Benzaldehyde.—Claisen (*Ber.*, 1890, **23**, 976) obtained ethyl cinnamate by the action of sodium on a mixture of ethyl acetate and benzaldehyde. Stobbe (*Ber.*, 1894, **27**, 2405), using ethyl succinate, obtained ethyl phenylitaconate. R. Fittig (*Annalen*, 1894, **282**, 334) prepared benzylideneglutaric acid by acting on a mixture of equal molecules of glutaric acid and benzaldehyde. In the author's experiments, 26·5 grams (1 mol.) of ethyl phenylglycinoacetate were dissolved in 100 grams of anhydrous benzene; then 2·3 grams of sodium (1 atom) as wire were introduced in the cold, and to this were added 10·6 grams (1 mol.) of freshly distilled benzaldehyde. After some 20 minutes, the mixture became brown, much heat was developed, and an energetic reaction took place, which was moderated by cooling. After a few hours, all the sodium had disappeared and the mixture became very dark. Water was now added and the benzene separated from the aqueous layer. The benzene portion was shaken with water until the aqueous extract no longer gave a precipitate with hydrochloric acid. The aqueous part is then cleared by shaking with a little ether, and finally purified by aspiration. On passing a stream of carbon dioxide through the solution, a light yellow substance was precipitated, and of this 12 grams were obtained. A second precipitate was produced on adding hydrochloric acid to the filtrate, which proved to be identical with the first. The total crude product, which weighed 29 grams, tended to decompose, and after two or three days it became

pasty and a gas was evolved. The substance is soluble in alcohol, benzene, and chloroform, but does not crystallise very readily from any of these solvents; the alcoholic solutions yield prismatic plates, and aqueous alcohol gives needles melting at 137—138°.

This substance, when pure, is light yellow; it dissolves with difficulty in cold aqueous sodium carbonate, but readily on warming, and it is reprecipitated unchanged on the addition of acid. After heating with water, the solution acquires an acid reaction, indicating the possibility of the substance being a lactone. The alcoholic solution gives a brownish-red coloration with ferric chloride. No coloured product was obtained by fusion with caustic potash and subsequent treatment with water, hydrochloric acid, and ferric chloride. When heated up to 160°, the substance loses carbon dioxide, and a dark brown, viscous liquid remains behind.

0·2584 gave 0·6633 CO_2 and 0·1404 H_2O. C = 70·02; H = 6·03.
0·2213 „ 0·5720 CO_2 „ 0·1167 H_2O. C = 70·47; H = 5·86.
0·1780 „ 6·8 c.c. nitrogen at 12° and 757 mm. N = 4·51.
$C_{19}H_{19}O_4N$ requires C = 70·15; H = 5·85; N = 4·31 per cent.

The properties of this substance are those of a lactone and its constitution is probably that shown on p. 436. The silver salt was obtained as a bulky, yellow precipitate which was collected and successively washed with water, alcohol, and ether, and dried in an exhausted desiccator. This salt was prepared several times, but it always contained too much silver, owing possibly to some reduction having taken place.

0·1697 gave 0·0459 Ag. Ag = 27·10.
0·1968 „ 0·0530 Ag. Ag = 26·96.
$C_{19}H_{20}O_5NAg$ and $C_{19}H_{18}O_4NAg$ require Ag = 24 and Ag = 25 per cent. respectively.

The calcium salt, obtained by heating an ammoniacal solution of the substance with a 20 per cent. solution of calcium chloride, has a yellow colour.

0·1912 gave 0·0162 CaO. Ca = 8·4.
$(C_{19}H_{18}O_4N)_2Ca$ requires Ca = 8·14 per cent.

A weighed amount of the pure substance was dissolved in chloroform and a solution containing 2·91 grams of bromine in 100 grams of this solvent added until the colour, which disappeared rapidly at first, became permanent. The amount added corresponded with 3 molecules of bromine, and hydrogen bromide was evolved. A white substance crystallised in needles (m. p. 175°). The filtrate left a very slight residue on evaporation.

0·1110 gave 0·1152 AgBr. Br = 44·15.

$C_{19}H_{14}O_3NBr_3$ requires Br = 44·11 per cent.

No insoluble product was obtained by shaking up an alkaline solution of the substance with benzoyl chloride. The compound was saponified by dissolving in alcohol and adding from 2 to 2½ times the theoretical amount of 50 per cent. caustic potash. After the solution had been left for a week, the potassium salt, which had separated in yellow needles, was collected and dissolved in water. Carbon dioxide was passed through the solution and acetic acid then added, but in neither case was a precipitate obtained, although the original substance is easily thrown down by both these reagents. However, on adding hydrochloric acid, a straw-coloured substance was deposited.

This acid is soluble in hot water, separating again on cooling; it is not easily recrystallised, but separates best from aqueous methyl alcohol. Boiling should be avoided as decomposition sets in; the acid melts and decomposes at 91—93°.

0·1239 gave 0·3102 CO_2 and 0·0584 H_2O. C = 68·26; H = 5·23.

0·1225 ,, 0·3073 CO_2 ,, 0·0584 H_2O. C = 68·44; H = 5·34.

$C_{17}H_{15}O_4N$ requires C = 68·68; H = 5·05 per cent.

0·1226 required 11·0 c.c. baryta solution [1 c.c. = 0·0032 $Ba(OH)_2$].

Found M. W. = 298. $C_{17}H_{15}O_4N$ requires M. W. = 297.

The acid is therefore monobasic and has the constitution

$$CO<\begin{matrix}O-CHPh\\CH_2\cdot NPh\end{matrix}>CH\cdot CO_2H.$$

Ethyl *o*-tolylglycinoacetate behaves similarly and yields an acid which crystallises from alcohol and melts at 165°.

Action of Ammonia on Ethyl Phenylglycinoacetate.—On adding an excess of concentrated ammonia solution (0·88) to an alcoholic solution of this ester, there separated after some time a white substance which melted at 238° and was insoluble in cold water, but readily soluble in acids. Ammonia is evolved on heating with caustic soda.

0·1852 gave 32·3 c.c. nitrogen at 14° and 744·5 mm. N = 20·10.

The diamide, $C_6H_5N(CH_2\cdot CO\cdot NH_2)_2$, requires N = 20·28 per cent.

Ethyl *o*-tolylglycinoacetate treated in the same way is at first deposited unchanged (m. p. 60°). When left for several days in contact with its mother liquor, the ester disappears, and on evaporation a white substance crystallises out in needles (m. p. 160—161°). This was found to have the same properties as the phenyl derivative.

0·1840 gave 29·0 c.c. nitrogen at 14° and 764·5 mm. N = 18·66.

The diamide, $C_7H_7\cdot N(CH_2\cdot CO\cdot NH_2)_2$, requires N = 19·0 per cent.

Condensation of Phenylglycinoacetic Esters with Oxalic Esters in Presence of Alkyloxides.

One molecular proportion of sodium in the form of wire was heated in a reflux apparatus with slightly more than the theoretical amount of absolute alcohol required to convert it into the ethoxide. A mixture of one molecule of each ester was gradually poured down the condenser, the liquid being gently heated. After an interval of from 5—20 minutes, depending on the ester used, an energetic reaction took place and the pasty mass became solid and was then heated on the water-bath for an hour. When cold, the solid mass was dissolved in water, a considerable amount of solvent being required owing to its insolubility. Any unchanged ester was extracted by shaking up with a little ether. On gradually adding dilute hydrochloric acid, the sodium salt was decomposed and the condensation product precipitated in the crude state. All the following substances are conveniently recrystallised from alcohol.

The Condensation of Ethyl Phenylglycinoacetate, Ethyl Oxalate, and Sodium Ethoxide.—This condensation was carried out many times with varying proportions and the product obtained was always the same, but only with the following proportions was the reaction complete: 2·3 grams of sodium (1 mol.) were heated with rather more than 4·6 grams (1 mol.) of absolute alcohol. To this was added a mixture of 13·25 grams (1 mol.) of ethyl phenylglycinoacetate and 7·3 grams (1 mol.) of ethyl oxalate. On treating the product in the manner described, 13—15 grams of substance were obtained, corresponding with an 80 per cent. yield. This substance recrystallises from alcohol in long, silky needles which are quite white after two crystallisations; it is very soluble in chloroform, but less readily so in glacial acetic acid, from which solvent it crystallises very well. The solubility in ether is slight, and from this solution are obtained small, brilliant crystals (m. p. 137°). The compound is insoluble in water or in sodium carbonate solution; cold aqueous caustic soda dissolves it, forming a yellow solution; it is insoluble in concentrated hydrochloric acid, but dissolves readily in concentrated sulphuric acid. An alcoholic solution of ferric chloride develops a dark greenish-blue coloration; silver nitrate is reduced at once in the cold. The barium salt is yellow, the copper salt greenish-blue, and the lead salt white.

An alcoholic solution was heated with phenylhydrazine dissolved in glacial acetic acid; in another experiment, the two compounds were heated directly together for varying times. In no case did condensation take place, the substance crystallising out unchanged. Negative results were also obtained with hydroxylamine and with the Schotten-

Baumann reaction. The substance was distilled under the ordinary pressure; it melted and almost at once emitted fumes which solidified in the receiver and in the side tube of the flask. This solid, when crystallised from alcohol, melted at 137°, and therefore consisted of the unaltered substance.

0·2585 gave 0·5734 CO_2 and 0·1240 H_2O. C = 60·49; H = 5·33.
0·2195 ,, 0·4823 CO_2 ,, 0·1078 H_2O. C = 59·97; H = 5·45.
0·1269 ,, 5·0 c.c. nitrogen at 14·5° and 753 mm.; N = 4·58.
$C_{16}H_{17}O_6N$ requires C = 60·19; H = 5·33; and N = 4·38 per cent.

This empirical formula gives a molecular weight 319. The substance must contain at least one atom of nitrogen, and the percentage of nitrogen found leads to a molecular weight of 306.

The substance was dissolved in 100 c.c. of alcohol and titrated against baryta [1 c.c. = 0·0065 $Ba(OH)_2$].

0·2030 gram of the substance required 17·0 c.c. for neutralisation, deducting 1 c.c. required by the alcohol. Equivalent weight = 157·5.

This result shows the acid to contain two hydroxyl groups and to have M. W. = 315. $C_{16}H_{17}O_6N$ requires M. W. = 319; 0·1158 dissolved in 18·83 benzene gave $\Delta t = 0·098°$ M. W. = 307·4.

The number of alkoxyl groups present in the molecule was determined by Zeisel's method. The substance used was that which was obtained from ethyl phenyglycinoacetate, methyl oxalate, and sodium methoxide, melting at 188°.

0·1909 gave 0·301 AgI. OMe = 20·8.
$C_{14}H_{13}O_6N$ requires OMe = 21·3 for two methoxyl groups.

No reaction takes place with phenylcarbimide in the cold but, on warming gently, a solution was obtained which remained clear for some time and slowly deposited white crystals on cooling. The precipitate was collected and recrystallised from aqueous alcohol (m. p. 169°). This substance possesses very different properties from the original. Ferric chloride no longer gives a coloration, and no yellow coloration is obtained with caustic soda in the cold; this only appears on boiling, when decomposition takes place and the odour of carbimide is observed. Silver nitrate is no longer reduced in the cold.

0·213 gave 12·1 c.c. nitrogen at 16° and 754 mm. N = 6·57.
$C_{23}H_{22}O_7N_2$ requires N = 6·39 per cent.

This result corresponds with the addition of 1 molecule of phenylcarbimide, and establishes the presence of at least one hydroxyl group.

The presence of hydroxyl groups is further shown by the fact that

if a solution of the substance is treated with a current of dry ammonia it is thrown out unchanged.

Some of the substance, dissolved in chloroform, was treated with a solution of bromine in the same solvent. The colour of the bromine disappeared rapidly at first, fumes of hydrogen bromide being abundantly evolved. The white, crystalline powder, which separated out slowly, was recrystallised from aqueous alcohol, and thus obtained in transparent needles melting at 119—120°. This substance, which was insoluble in caustic soda and gave no coloration with ferric chloride, was identified on analysis as tribromoaniline (m. p. 119°).

It was thought at the outset that the saponification of this substance would be readily brought about, but it was never accomplished. The substance was left for several days in contact with aqueous and alcoholic caustic potash. At other times, the mixture was heated for 3 hours. In every case, the potassium salt obtained yielded the original substance on acidifying. Acids were then tried, 0·65 gram of the compound being heated for 3 hours with 15 c.c. of concentrated hydrochloric acid. After cooling, the solid matter was collected and found to consist of the unaltered substance. The filtrate, on extraction with ether, yielded only a little tarry matter.

The analogous substances enumerated on p. 437 were prepared in the same manner and showed no difference in properties. Analyses of some of these are now given, and it will be seen that they are derived from the substance $C_{16}H_{17}O_6N$ by the replacement of one or more ethyl groups by methyl. Ethyl phenylglycinoacetate (13·25 grams), when condensed with 1 molecule of methyl oxalate in presence of sodium methoxide, yielded a substance which, after recrystallisation, melted at 188°.

0·2006 gave 0·4225 CO_2 and 0·0866 H_2O. C = 57·44 ; H = 4·79.
0·2249 „ 0·4768 CO_2 „ 0·0919 H_2O. C = 57·81 ; H = 4·54.
0·1944 „ 8·4 c.c. nitrogen at 14° and 740 mm. N = 4·94.
$C_{14}H_{13}O_6N$ requires C = 57·73 ; H = 4·47 ; N = 4·81 per cent.

This result corresponds with the replacement of two ethyl by two methyl groups.

By condensation of methyl phenylglycinoacetate with ethyl oxalate in presence of sodium methoxide, a substance melting at 188° is obtained, identical with that just described.

0·2133 gave 0·4539 CO_2 and 0·0931 H_2O. C = 58·03 ; H = 4·84.
0·275 gave 12·0 c.c. nitrogen at 14° and 769 mm. N = 4·81 per cent.

The third type of compound is illustrated by the condensation product melting at 175°, and obtained from ethyl phenylglycinoacetate and ethyl oxalate in the presence of sodium methoxide.

0·2276 gave 0·4888 CO_2 and 0·1033 H_2O. C = 58·57; H = 5·04.
0·2402 „ 0·5202 CO_2 „ 0·1020 H_2O. C = 59·06; H = 4·72.
0·4970 „ 18·2 c.c. nitrogen at 16° and 770 mm. N = 4·33.
$C_{15}H_{15}O_6N$ requires C = 59·04; H = 4·91; N = 4·58 per cent.

The substance is derived from the original $C_{16}H_{17}O_6N$ by the substitution of one methyl for one ethyl group.

Of the other products, two are identical, melt at 147—148°, and have the formula $C_{15}H_{15}O_6N$. The remaining two have the formula $C_{14}H_{13}O_6N$, one melting at 195° and the other at 159°.

For the sake of comparison, 14 grams of ethyl *o*-tolylglycinoacetate were condensed with 6·5 grams of ethyl oxalate in presence of sodium ethoxide. The recrystallised product melted at 146°.

0·3477 gave 12·7 c.c. nitrogen at 15° and 765 mm. N = 4·30.
$C_{17}H_{19}O_6N$ requires N = 4·20 per cent.

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LVI.—*An Asymmetric Synthesis of Quadrivalent Sulphur.*

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WHEN an asymmetric atom is produced in a molecule in presence of an optically active complex, two isomerides may be formed, and the question has arisen whether any preference is shown to the formation of either of these. The problem has attracted much attention in the last few years, but hitherto the reactions which have been examined have dealt with asymmetric carbon; it therefore seemed of interest to study the matter in connection with other elements which are capable of acting as centres of optical activity. The present communication contains an account of some experiments dealing with the asymmetric synthesis of sulphur compounds.

The substances chosen for this investigation were thetine esters, a class of compound which has been but little studied. Indeed, it

seems that the only representative known is the ethyl ester of dimethylthetine prepared by Letts and Collie from dimethyl sulphide and ethyl bromoacetate (*Trans. Edin. Roy. Soc.*, 1878, **28**, 618).

The menthyl ester of bromoacetic acid unites with the alkyl sulphides at the ordinary temperature, but the reaction proceeds very slowly and even with methyl sulphide is scarcely complete after a week. The product of the reaction is the menthyl ester of a thetine bromide, $R_2SBr{\cdot}CH_2{\cdot}CO_2{\cdot}C_{10}H_{19}$.

Perhaps the only property of these menthyl esters of thetine which is worthy of special mention is the tendency which they show to break up into alkyl sulphide and menthyl bromoacetate. The ease with which this decomposition takes place varies according to the complexity of the alkyl groups united to the sulphur atom; the more complex the group, the more readily does decomposition take place. Of the three derivatives which have been examined, the dimethylthetine is by far the most stable, for it may be kept for several weeks without any change taking place; the diethylthetine, on the other hand, begins to decompose in a few days.

In solution, the dissociation into alkyl sulphide and ethyl bromoacetate proceeds even more readily, but it is affected by the nature of the solvent. The ethyl ester of diethylthetine bromide dissolves readily in water, giving solutions which show a characteristic behaviour. Strong solutions of this salt are quite transparent, but when warmed or diluted they become opaque owing to the separation of the sulphide and ethyl bromoacetate. Solutions of the thetine esters in epichlorohydrin are exceedingly unstable and can only be kept for a few hours without change; in alcohol, too, the diethylthetine may be almost completely resolved into its constituents by leaving the solution for some weeks.

It can be seen by comparing the behaviour of the dimethyl and diethyl derivatives that an increase in the size of the alkyl groups from methyl to ethyl causes a marked decrease in the stability of the thetine. This shows that the instability of the diethylthetine ester is at least partly due to steric influences, although to what extent it is impossible to say.

Wedekind ("Zur Stereochemie des Fünfwertigen Stickstoffes," Leipzig, 1899) has pointed out a similar instability in the case of phenylbenzylmethylallylammonium iodide, the aqueous solutions of which decompose when boiled into benzyl iodide and tertiary amine; Pope also (Trans., 1901, **79**, 828) has ascribed the autoracemisation of the dextrorotatory iodide to the same cause.

Such instability is not shown by all the salts of these bases, for example, the nitrates, when boiled in aqueous solution, are gradually saponified into menthol and the free thetine salt; the amount of

sulphide formed is quite small, and with the dimethylthetine ester only amounts to a trace.

The hydroxides of the menthyl esters of the thetines have only been obtained as oils which dissolve quite readily in water giving strongly alkaline solutions. After a short time, the alkalinity disappears, menthol separates out, and the free thetine remains in solution; this reaction may be expressed by the equation:

$$R_2{:}S(OH)\cdot CH_2\cdot CO_2\cdot C_{10}H_{19} = R_2{:}S{<}{\overset{-O-}{\underset{CH_2}{}}}{>}CO + C_{10}H_{19}\cdot OH.$$

The *l*-methyl ester of methylethylthetine bromide was prepared from methyl ethyl sulphide and *l*-menthyl bromoacetate. The most direct method of ascertaining whether the esters of dextro- and lævo-thetines have been produced in equal amount is to isolate the thetine, $\frac{CH_3}{C_2H_5}{>}S{<}{\overset{-O-}{\underset{CH_2}{}}}{>}CO$, from the synthetical product and examine its optical condition. With this object, the menthyl nucleus was eliminated in two ways: (*a*) by intramolecular saponification of the hydroxide and (*b*) by saponifying the ester with concentrated hydrochloric acid at the ordinary temperature. Both these methods yielded an inactive thetine, hence it would seem that the two isomerides are produced in equal quantity. These experiments, however, scarcely permit of a definite conclusion, for it is quite conceivable that any optically active thetine might be racemised during the process of saponification; but at the same time such a racemisation of optically quadrivalent sulphur has never been observed, indeed it would seem from Pope's experiments (Trans., 1900, **77**, 1074) that the activity of methylethylthetine is not destroyed by concentrated hydrochloric acid.

Further evidence was sought for by comparing the molecular rotations of the dimethyl- and diethyl-thetine bromides with that of the methyl ethyl derivative. The rotatory powers of these substances were determined in absolute alcohol, acetone, and in a mixture of equal volumes of alcohol and water. The concentration of the solutions examined varied between two and five per cent.; within those limits, the rotatory power of the thetine esters does not alter much. The temperature at which most of the measurements were made was 23°; variations of a degree on either side do not affect the rotation beyond the limit of experimental error. The values which are given in the following table are the molecular rotations of the three derivatives, and in most cases they are the mean of several observations with different specimens.

Molecular Rotations of the Menthyl Ester of the Thetine Bromides.

Solvent.	Substance.			Calculated mean.
	Dimethyl.	Diethyl.	Methyl ethyl.	
Alcohol and water......	−162·7°	−176·8°	−168·9°	−169·7°
Alcohol	157·9	169·0	162·7	163·4
Acetone	159·2	172·1	166·2	165·4

The platinichlorides of these bases are crystalline solids, and are more easily purified than the hygroscopic bromides. Pope has shown (Trans., 1900, **77**, 1074) that the activity of methylethylthetine still persists on conversion into the platinichloride; hence, for purposes of comparison, the platinichlorides should serve equally well as the bromides. The next table shows the molecular rotations of the three platinichlorides dissolved in epichlorohydrin.

Molecular Rotations of the Platinichlorides.

Dimethyl.	Diethyl.	Methyl ethyl.	Calculated mean.
−371·3°	−331·9°	−351·0°	−351·6°
2 × 185·6	2 × 165·8	2 × 175·5	2 × 175·8

In both tables, the last column represents the arithmetical mean between the experimental values for the dimethyl and diethyl derivatives, and it is evident that this calculated value lies fairly close to that found for the methylethylthetine.

So far as the author is aware, no homologous series of this particular type has been investigated; a large number of other series have been examined, but they consist for the greater part of homologous esters and allied substances, and it is only in a few of these that a certain regularity of rotatory power occurs in the lower members. It is therefore impossible to predict with certainty that the rotation of the *l*-menthyl ester of *dl*-methylethylthetine would lie intermediate between those of the two adjacent homologues. In spite of this, the evidence points to the conclusion that the two isomerides have been produced in equal amount, for the alternative carries with it the improbable assumption that the excess of one of the isomerides should adjust the discrepancy between the rotation of the *l*-menthyl ester of *dl*-methylethylthetine and the mean of the rotations of the dimethyl and diethyl derivatives.

Finally, the question was attacked in a more direct manner. The

acid bromide of *dl*-methylethylthetine bromide was prepared from bromoacetyl bromide and methyl ethyl sulphide, and subsequently converted into the menthyl ester by treatment with menthol. The product, the *l*-menthyl ester of *dl*-methylethylthetine bromide, was oily and evidently contained impurities; it was therefore converted into the insoluble platinichloride. The molecular rotation of the *l*-menthyl ester of *dl*-methylethylthetine platinichloride prepared in this manner was found to be $-350°$, a value almost identical with that obtained for the platinichloride, which was made from the product of asymmetric synthesis.

The evidence afforded by these three lines of research points in one direction, and, when considered all together, leads to the conclusion that the two isomeric *l*-menthyl esters of *l*- and *d*-methylethylthetine bromides are produced in equal amount during their synthesis from *l*-menthyl bromoacetate and methyl ethyl sulphide

Experimental.

l-*Menthyl Bromoacetate*, $CH_2Br \cdot CO_2 \cdot C_{10}H_{19}$ (*l*).—Forty grams of bromoacetyl bromide were gradually added to a solution of thirty grams of menthol in two hundred c.c. of chloroform, and the mixture heated on a water-bath until the evolution of hydrogen bromide ceased. After being washed with water and dilute aqueous sodium carbonate, the solution was dried over calcium chloride and then fractionated. Fifty-two grams of the liquid distilled between 140° and 145° under 12 mm. pressure. Redistillation of this portion yielded *l*-menthyl bromoacetate as a colourless oil boiling at 144—145° under 12 mm. pressure.

0·464 gave 0·3146 AgBr. Br = 28·92.
0·3682 ,, 0·6948 CO_2 and 0·2531 H_2O. C = 52·17 ; H = 7·7.
$C_{12}H_{21}O_2Br$ requires C = 51·98 ; H = 7·58 ; Br = 28·88 per cent.

A determination of the density gave $d 25°/4° = 1·208$, and when examined in the polariscope it was found that $\alpha_D - 18·72°$ when $l = 0·25$ dcm. and $t = 25°$, whence $[\alpha]_D - 61·98°$ and $[M]_D - 171·6°$.

In alcoholic solutions, α was found to be $-7·60°$ when $l = 1$dcm., $c = 12·21$, and $t = 24°$, whence $[\alpha]_D - 62·24°$ and $[M]_D - 172·4°$.*

Another sample of the ester prepared in the same way gave $\alpha_D - 7·61°$ with $l = 1$ dcm., $c = 12·2$, and $t = 22°$, whence $[\alpha]_D - 62·3°$ and $[M]_D - 172·5°$.

The menthol used in this preparation was obtained from Kahlbaum

* Tschugaeff (*J. Russ. Phys. Chem. Soc.*, 1902, **34**, 606) has given $d 20°/4° = 1·2136$, $[\alpha]_D - 60·95°$, and $[M] - 168·8°$.

and gave $[\alpha]_D - 10{\cdot}05°$ at 22° when $l = 2$ dcm. and $c = 10{\cdot}0$, whence $[\alpha]_D - 50{\cdot}2°$.*

The ester, when saponified with cold dilute alcoholic potash, gave a menthol which showed $[\alpha]_D - 3{\cdot}98°$ when l = 1dcm., $c = 8{\cdot}0$, and $t = 21°$, whence $c - 49{\cdot}7°$; thus it seems that the above process of esterification does not appreciably alter the optical condition of the menthol.

A sample of the ester was also prepared from menthol, bromoacetic acid, and concentrated sulphuric acid ; it showed $[\alpha]_D - 56{\cdot}4°$, a number which is considerably below that given by the ester prepared from the acid bromide.

l-*Menthyl Ester of Dimethylthetine Bromide*, $\frac{CH_3}{C_2H_5}>S<\frac{CH_2{\cdot}CO_2{\cdot}C_{10}H_{19}}{Br}$.

Ten grams of methyl sulphide were mixed with 20 grams of *l*-menthyl bromoacetate. In the course of 24 hours the liquid became cloudy, and at the end of a week had completely solidified to a colourless mass of crystals. After being washed with ether and thoroughly dried in a desiccator the product weighed 20 grams; theory requires 27 grams.

By dissolving in absolute alcohol and precipitating the solution with ether, the *l*-menthyl ester of dimethylthetine bromide is deposited in the form of colourless leaflets, which decompose at 87—90°, according to the rapidity of heating. The thetine ester is very soluble in absolute alcohol, moderately in acetone, and sparingly so in water ; when any of these solutions are warmed or allowed to remain at the ordinary temperature, decomposition into methyl sulphide and menthyl bromoacetate takes place. By allowing an alcoholic solution to evaporate slowly, this substance may be obtained in the form of prisms fully 1 cm. in length.

0·288 gave 0·1561 AgBr. Br = 23·07.

$C_{14}H_{27}O_2BrS$ requires Br = 23·6 per cent.

The halogen was estimated by precipitation with silver nitrate from an aqueous solution of the bromide, and the deficiency in the percentage of bromine is without doubt due to dissociation of the dissolved substance. The same behaviour is shown by the dimethyl and diethyl derivatives.

When examined in the polariscope, dimethylthetine *l*-menthyl ester bromide gave the following results.

In a mixture of equal volumes of absolute alcohol and water :

$\alpha_D - 1{\cdot}24°$ when $c = 2{\cdot}568$, $t = 22°$, and $l = 1$ dcm., whence $[\alpha]_D - 48{\cdot}4°$ and $[M]_D - 164{\cdot}0°$.

* Arth (*Ann. Chim. Phys.*, 1886, [vi], 7, 438) gives $[\alpha]_D - 50{\cdot}1°$, $c = 10$, and $t = 18°$.

$\alpha_D - 1{\cdot}12^\circ$ when $c = 2{\cdot}352$, $t = 23^\circ$, and $l = 1$ dcm., whence $[\alpha]_D - 47{\cdot}6^\circ$ and $[M]_D - 161{\cdot}3^\circ$.

$\alpha_D - 2{\cdot}34^\circ$ when $c = 4{\cdot}838$, $t = 24^\circ$, and $l = 1$ dcm., whence $[\alpha]_D - 48{\cdot}3^\circ$ and $[M]_D - 163{\cdot}7^\circ$.

$\alpha_D - 1{\cdot}00^\circ$ when $c = 2{\cdot}09$, $t = 24^\circ$, and $l = 1$ dcm., whence $[\alpha]_D - 47{\cdot}8^\circ$ and $[M]_D - 162{\cdot}0^\circ$.

In absolute alcohol:

$\alpha_D - 1{\cdot}03^\circ$ when $c = 2{\cdot}218$, $t = 23^\circ$, and $l = 1$ dcm., whence $[\alpha]_D - 46{\cdot}4^\circ$ and $[M]_D - 157{\cdot}3^\circ$.

$\alpha_D - 0{\cdot}92^\circ$ when $c = 1{\cdot}982$, $t = 24^\circ$, and $l = 1$ dcm., whence $[\alpha]_D - 46{\cdot}4^\circ$ and $[M]_D - 157{\cdot}3^\circ$.

$\alpha_D - 2{\cdot}51^\circ$ when $c = 5{\cdot}34$, $t = 23^\circ$, and $l = 1$ dcm., whence $[\alpha]_D - 47{\cdot}0^\circ$ and $[M]_D - 159{\cdot}3^\circ$.

In acetone:

$\alpha_D - 1{\cdot}99^\circ$ when $c = 4{\cdot}156$, $t = 24^\circ$, and $l = 1$ dcm., whence $[\alpha]_D - 47{\cdot}3^\circ$ and $[M]_D - 160{\cdot}8^\circ$.

$\alpha_D - 0{\cdot}82^\circ$ when $c = 1{\cdot}756$, $t = 23^\circ$, and $l = 1$ dcm., whence $[\alpha]_D - 46{\cdot}7^\circ$ and $[M]_D - 158{\cdot}3^\circ$.

A freshly prepared solution in epichlorohydrin gave $\alpha_D - 1{\cdot}65^\circ$ when $c = 1{\cdot}808$, $t = 22^\circ$, and $l = 2$ dcm., whence $[\alpha]_D - 45{\cdot}6^\circ$ and $[M]_D - 154{\cdot}6^\circ$. After 48 hours, this solution smelt strongly of dimethyl sulphide, and showed $[\alpha]_D - 37{\cdot}6^\circ$.

Another solution in the same solvent when freshly made gave $\alpha_D - 1{\cdot}23^\circ$ when $c = 2{\cdot}75$, $t = 23^\circ$, and $l = 1$ dcm., whence $[\alpha]_D - 44{\cdot}7^\circ$ and $[M]_D - 151{\cdot}7^\circ$.

The *chloride* was not isolated; it was made by shaking a solution of the bromide in alcohol and water with excess of silver chloride. The filtrate showed the same rotation when examined in a 1-dcm. tube as the solution of the bromide from which it was prepared, hence the molecular rotation of the chloride is the same as that of the bromide and lies at about -163°.

The *aurichloride*, $S(CH_3)_2Cl{\cdot}CH_2{\cdot}CO_2{\cdot}C_{10}H_{19},AuCl_3$, obtained as a yellow, crystalline precipitate from solutions of the chloride, is soluble in chloroform, alcohol, and acetone, but is insoluble in water and carbon disulphide, and when exposed to the air oxidises to a brown substance, which is insoluble in chloroform. The aurichloride was purified by dissolving in acetone and precipitating with water; after drying under diminished pressure, it melted at 124—125°.

0·1619 gave 0·0533 Au. Au = 32·92.

$C_{14}H_{27}O_2ClS,AuCl_3$ requires Au = 32·97 per cent.

When dissolved in acetone and examined in the polariscope it gave

$a_D - 0{\cdot}89°$ when $c = 2{\cdot}957$, $t = 22°$, and $l = 1$ dcm., whence $[a]_D - 30{\cdot}1°$ and $[M]_D - 180{\cdot}0°$.

The *platinichloride*, $[S(CH_3)_2Cl{\cdot}CH_2{\cdot}C_{10}H_{19}]_2.PtCl_4$, is precipitated from solutions of the chloride as a pale yellow, crystalline powder, which is insoluble in the usual organic media, but sparingly soluble in epichlorohydrin. It melts at 177° with decomposition.

0·1143 gave 0·0239 Pt. Pt = 20·9.
0·2057 „ 0·1903 AgCl. Cl = 22·8.
0·1557 „ 0·0794 $BaSO_4$. S = 7·0.
$(C_{14}H_{27}O_2SCl)_2,PtCl_4$, requires Pt = 21·04 ; Cl = 23·0 ; S = 6·9 per cent.

The optical constants of the platinichloride were found to be as follows:

$a_D - 0{\cdot}38°$ when $c = 0{\cdot}9468$, $t = 22°$, and $l = 1$ dcm., whence $[a]_D - 40{\cdot}1°$ and $[M]_D - 371{\cdot}3°$.

$a_D - 0{\cdot}37°$ when $c = 0{\cdot}9224$, $t = 21°$, and $l = 1$ dcm., whence $[a]_D - 40{\cdot}1°$ and $[M]_D - 371{\cdot}3°$.

The *hydroxide* was prepared by the action of silver oxide on an alcoholic solution of the bromide ; the filtrate from the silver bromide was strongly alkaline, and, when precipitated with ether, yielded the substance as an oil. Aqueous solutions of this base decompose gradually at the ordinary temperature, giving menthol and dimethylthetine.

The *nitrate*, which crystallises from hot aqueous solutions in the form of colourless needles, is the most stable of those salts which have been examined.

dl-*Methylethylthetine* l-*Menthyl Ester Bromide*,

$$\begin{matrix} CH_3 \\ C_2H_5 \end{matrix} > S < \begin{matrix} CH_2{\cdot}CO_2{\cdot}C_{10}H_{19} \\ Br \end{matrix}.$$

A mixture of 10 grams of methyl ethyl sulphide and 20 grams of *l*-menthyl bromoacetate was allowed to remain for a week ; the solid product was then broken up, and, after being well washed with dry ether, was dissolved in alcohol and reprecipitated. This treatment yielded 15 grams of methylethylthetine *l*-menthyl ester bromide in the form of colourless needles, which melted at 80—82° with decomposition. In distinction from the dimethyl derivative, the methylethylthetine is hygroscopic, and can only be obtained pure by using carefully dried reagents. When examined in the polariscope, it showed the following behaviour.

In a mixture of equal volumes of alcohol and water :

$a_D - 2{\cdot}14°$ when $c = 4{\cdot}46$, $t = 22°$, and $l = 1$ dcm., whence $[a]_D - 48{\cdot}0°$ and $[M]_D - 169{\cdot}4°$.

α_D $-2{\cdot}09°$ when $c = 4{\cdot}349$, $t = 23°$, and $l = 1$ dcm., whence $[\alpha]_D$ $-48{\cdot}0°$ and $[M]_D$ $-169{\cdot}4°$.

α_D $-2{\cdot}38°$ when $c = 5{\cdot}0$, $t = 23°$, and $l = 1$ dcm., whence $[\alpha]_D$ $-47{\cdot}6°$ and $[M]_D$ $-168{\cdot}0°$.

In absolute alcohol:

α_D $-1{\cdot}29°$ when $c = 2{\cdot}784$, $t = 23°$, and $l = 1$ dcm., whence $[\alpha]_D$ $-46{\cdot}3°$ and $[M]_D$ $-163{\cdot}4°$.

α_D $-2{\cdot}37°$ when $c = 5{\cdot}135$, $t = 23°$, and $l = 1$ dcm., whence $[\alpha]_D$ $-46{\cdot}1°$ and $[M]_D$ $-162{\cdot}7°$.

α_D $-2{\cdot}29°$ when $c = 4{\cdot}989$, $t = 23°$, and $l = 1$ dcm., whence $[\alpha]_D$ $-45{\cdot}8°$ and $[M]_D$ $-162{\cdot}0°$.

In acetone:

α_D $-1{\cdot}93°$ when $c = 4{\cdot}095$, $t = 22°$, and $l = 1$ dcm., whence $[\alpha]_D$ $-47{\cdot}1°$ and $[M]_D$ $-166{\cdot}2°$.

A freshly prepared solution in epichlorohydrin gave α_D $-1{\cdot}61°$ when $c = 3{\cdot}829$, $t = 22°$, and $l = 1$ dcm., whence $[\alpha]_D$ $-42{\cdot}0°$ and $[M]_D$ $-148{\cdot}2°$.

Another solution gave α_D $-1{\cdot}57°$ when $c = 3{\cdot}661$, $t = 21°$, and $l = 1$ dcm., whence $[\alpha]_D$ $-42{\cdot}8°$ and $[M]_D$ $-150{\cdot}8°$.

Saponification of dl-*Methylethylthetine* l-*Menthyl Ester Bromide.*

(*a*) With concentrated hydrochloric acid:

The bromide was dissolved in strong hydrochloric acid and set aside for 6 days at the ordinary temperature; water was then added and the mixture repeatedly extracted with ether. After several extractions, the aqueous portion was examined in the polariscope and found to be inactive. It was evaporated to dryness under diminished pressure, and then, after being redissolved in alcohol, was treated with excess of silver chloride. The filtrate from the silver halide was acidified with hydrochloric acid and precipitated with platinic chloride. When dry, the precipitate was analysed:

0·3506 gave 0·1009 Pt. Pt = 28·77.

$(C_5H_{11}O_2SCl)_2,PtCl_4$ requires Pt = 28·74 per cent.

The platinum salt is evidently that of methylethylthetine; when examined in the polariscope it was found to be inactive.

(*b*) With silver oxide:

An aqueous solution of the above methylethylthetine menthyl ester was mixed with excess of silver oxide and left for 3 days at the ordinary temperature. The solution, after being filtered and repeatedly extracted with ether, was inactive; the platinic chloride of

methylethylthetine, prepared from the solution in the usual way, was also without action on polarised light.

(*c*) A third saponification was carried out with thionyl chloride; the result was as before, an inactive methylethylthetine being produced.

The *platinichloride*, $\left(\begin{matrix}CH_3\\C_2H_5\end{matrix}>S<\begin{matrix}CH_2\cdot CO_2\cdot C_{10}H_{19}\\Cl\end{matrix}\right)_2, PtCl_4$, obtained as an orange-buff precipitate by adding platinic chloride to aqueous solutions of the chloride, melts at 173—174° and may be crystallised from hot acetone, in which it is sparingly soluble; it is also soluble in epichlorohydrin, but is insoluble in alcohol, water, and other common solvents. The specimens used for examination in the polariscope were not recrystallised, but purified by thoroughly washing the original precipitate with cold acetone.

0·3987 substance gave 0 0817 Pt. Pt = 20·49.
0·1300 " " 0·1188 AgCl. Cl = 22·5.
0·1519 " " 0·0752 $BaSO_4$. S = 6·8.
$(C_{15}H_{29}O_2SCl)_2,PtCl_4$ requires Pt = 20·4; Cl = 22·3; S = 6·7 per cent.

When dissolved in epichlorohydrin, the double salt gave α_D − 1·17° when c = 3·158, t = 22°, and l = 1 dcm., whence $[\alpha]_D$ − 37·0° and $[M]_D$ − 352·9°; α_D − 0·85° when c = 2·323, t = 21°, and l = 1 dcm., whence $[\alpha]_D$ − 36·6° and $[M]_D$ − 349·1°.

As already mentioned in the introduction, this platinichloride was prepared in a different way. Bromoacetyl bromide was mixed with excess of methyl ethyl sulphide and set aside during four days in a flask protected from moisture. An oily layer was deposited, presumably the acid bromide of methylethylthetine; it was separated from excess of sulphide, washed with dry ether, and mixed with rather less than the calculated amount of menthol. After being kept for several days in a dry atmosphere, the oily thetine ester was washed with ether, dissolved in a small quantity of water, and again extracted with ether to remove menthol and any remaining sulphide. The aqueous solution, which now contained the menthyl ester of the thetine and probably a considerable quantity of methylethylthetine bromide, was treated with silver chloride and precipitated with platinic chloride. The precipitate was collected and after purification was analysed:

0·4532 gave 0·0936 Pt. Pt = 20·65.
$(C_{15}H_{29}O_2SCl)_2,PtCl_4$ requires Pt = 20·44 per cent.

When dissolved in epichlorohydrin and examined in the polariscope it gave:

α_D − 0·90° when c = 2·45, t = 23°, and l = 1 dcm., whence $[\alpha]_D$ − 36·7° and $[M]_D$ − 350·0°.

l-*Menthyl ester of diethylthetine bromide*, $S(C_2H_5)_2Br\cdot CH_2\cdot CO_2\cdot C_{10}H_{19}$, was obtained by a similar method to that employed in the preparation of the dimethyl and methyl derivatives. In one experiment, fifteen grams of *l*-menthyl bromoacetate and ten grams of ethyl sulphide yielded twelve grams of crude thetine bromide. The pure substance forms long, colourless needles which melt at 73—74° if rapidly heated and which are very soluble in water and alcohol. Owing to the instability of this substance, it was found necessary to employ freshly prepared specimens for analysis and determination of rotatory power. When the halogen was estimated in solutions by precipitation with silver nitrate, the results were always about 0·5—0·8 per cent. less than the calculated value; a determination of halogen by Carius' method gave the following result:

0·4779 gave 0·248 AgBr. Br = 22·0.

$C_{15}H_{31}O_2BrS$ requires Br = 21·8 per cent.

When dissolved in a mixture of alcohol and water in equal volumes, the diethylthetine ester gave $\alpha_D - 1·38°$ when $c = 2·88$, $t = 22°$, and $l = 1$ dcm., whence $[\alpha]_D - 47·8°$ and $[M]_D - 175·4°$.

$\alpha_D - 2·47°$ when $c = 5·08$, $t = 23°$, and $l = 1$ dcm., whence $[\alpha]_D - 48·5°$ and $[M]_D - 177·9°$.

$\alpha_D - 1·16°$ when $c = 2·39$, $t = 23°$, and $l = 1$ dcm., whence $[\alpha]_D - 48·5°$ and $[M]_D - 177·9°$.

$\alpha_D - 2·11°$ when $c = 4·393$, $t = 23°$, and $l = 1$ dcm., whence $[\alpha]_D - 48·0°$ and $[M]_D - 176·1°$.

In absolute alcohol:

$\alpha_D - 2·34°$ when $c = 5·057$, $t = 22°$, and $l = 1$ dcm., whence $[\alpha]_D - 46·2°$ and $[M]_D - 169·5°$.

$\alpha_D - 1·07°$ when $c = 2·33$, $t = 22°$, and $l = 1$ dcm., whence $[\alpha]_D$ 45·9° and $[M]_D - 168·4°$.

$\alpha_D - 1·12°$ when $c = 2·426$, $t = 22°$, $l = 1$ dcm., whence $[\alpha]_D - 46·1°$ and $[M]_D - 164·2°$.

In acetone:

$\alpha_D - 2·11°$ when $c = 4·497$, $t = 22°$, and $l = 1$ dcm., whence $[\alpha]_D - 46·9°$ and $[M]_D - 172·1°$.

A fresh solution in epichlorohydrin gave $\alpha_D - 1·25°$ when $c = 3·043$, $t = 21°$, and $l = 1$ dcm., whence $[\alpha]_D - 41·0°$ and $[M]_D - 150·4°$; after four days, $[\alpha]_D$ had sunk to $- 38·4°$.

The *platinichloride*, $\left(\begin{matrix}C_2H_5\\C_2H_5\end{matrix}>S<\begin{matrix}CH_2\cdot CO_2\cdot C_{10}H_{19}\\Cl\end{matrix}\right)_2,PtCl_4$, forms buff-coloured needles which melt at 148—149° with decomposition; it is very soluble in acetone and in epichlorohydrin, sparingly so in cold ethyl acetate, and insoluble in water. Analysis gave the following data:

0·0974 gave 0·0193 Pt. Pt = 19·8.
0·1156 „ 0·1000 AgCl. Cl = 21·4.
0·1156 „ 0·0494 $BaSO_4$. S = 6·5.
$(C_{16}H_{31}O_2ClS)_2,PtCl_4$ requires Pt = 19·84 ; Cl = 21 6 ; S = 6·5 per cent.

It was found that when dissolved in epichlorohydrin :

a_D − 0·70° when c = 2·093, t = 24°, and l = 1 dcm., whence $[a]_D$ − 33·9° and $[M]_D$ − 332·9°.

a_D − 0·46° when c = 1·363, t = 24°, and l = 1 dcm., whence $[a]_D$ − 33·7° and $[M]_D$ − 330·9°.

In acetone :

a_D − 0·61° when c = 1·709, t = 22°, and l = 1 dcm., whence $[a]_D$ − 35·7° and $[M]_D$ − 350·4°

At present, the investigation is being extended to other substances of a type similar to those described in this paper.

In conclusion, the author desires to thank Professor Collie for much valuable help and suggestion given while carrying out these experiments.

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LVII.—*The Combination of Mercaptans with Unsaturated Ketonic Compounds.*

By SIEGFRIED RUHEMANN.

LATELY (Trans., 1905, **87**, 17) I have shown that, under the influence of sodium ethoxide or piperidine, olefinic ketonic compounds combine with mercaptans to yield additive products. The further study of this reaction seemed to be advisable, because Posner, on using as catalytic agent hydrogen chloride either alone or in conjunction with zinc chloride, frequently obtained mixtures, since the mercaptans, besides acting additively at the ethylenic linking, partly condensed also with the ketonic group of the olefinic ketones. Thus Posner (*Ber.*, 1902, **35**, 809) found that *iso*amyl mercaptan on treatment with benzylideneacetophenone yielded an oil which, from a sulphur determination, he concluded was a mixture, and which on oxidation with

potassium permanganate furnished a small quantity of the sulphone, $C_6H_5 \cdot CH(SO_2 \cdot C_5H_{11}) \cdot CH_2 \cdot CO \cdot C_6H_5$. As shown in this paper, on employing piperidine as catalytic agent, there is thus formed the additive compound, *iso*amylthiolbenzylacetophenone,

$$C_6H_5 \cdot CH(S \cdot C_5H_{11}) \cdot CH_2 \cdot CO \cdot C_6H_5,$$

which melts at 49—50°. In my former communication (*loc. cit.*), the action of mercaptans on various mono-olefinic ketonic compounds containing the grouping $-\overset{|}{C}H\colon CH \cdot CO-$ has been described; I have since applied this reaction to several other members of this type of ketones, namely, benzylidenedeoxybenzoin and ethyl benzylidene-benzoylacetate. The behaviour, also, of piperidine towards a mixture of phenyl mercaptan and bromobenzylideneacetophenone, $C_6H_5 \cdot CBr\colon CH \cdot CO \cdot C_6H_5$, has been studied, with the unexpected result that phenylthiolbenzylacetophenone is formed, identical with the substance which is produced by the union of phenyl mercaptan with benzylideneacetophenone.

I have previously (*loc. cit.*) shown that cinnamylideneacetophenone, the di-olefinic ketone of the type $-\overset{|}{C}\colon \overset{|}{C} \cdot \overset{|}{C}\colon \overset{|}{C} \cdot CO-$, unites with one molecule only of a mercaptan, and that this result differs from Posner's statement (*Ber.*, 1904, **37**, 509), according to which this ketone forms additive products with two molecules of mercaptans. Prof. Posner has since, by letter, recognised the error and confirmed my result that the compound which is formed from cinnamylidene-acetophenone and phenyl mercaptan has the formula

$$C_6H_5 \cdot CH\colon CH \cdot CH(S \cdot C_6H_5) \cdot CH_2 \cdot CO \cdot C_6H_5.$$

After having established the behaviour of mercaptans towards this di-olefinic ketone, it seemed probable that Posner's statement as to the action of mercaptans on cinnamylideneacetone was also not correct. In his paper (*loc. cit.*), he records the experimental results of one of his pupils who thus has obtained oils which he has been able to transform into disulphones, whilst he has failed in producing a sulphone on oxidising the additive compound of benzylideneaceto-phenone with phenyl mercaptan. I have found, indeed, that my view is correct, for cinnamylideneacetone unites with one molecule only of phenyl mercaptan to yield the substance

$$C_6H_5 \cdot CH\colon CH \cdot CH(S \cdot C_6H_5) \cdot CH_2 \cdot CO \cdot CH_3,$$

which is not an oil, but a solid melting at 53—54°.

In the light of these results, it may be expected that cinnamylidene-benzylideneacetone, $C_6H_5 \cdot CH\colon CH \cdot CH\colon CH \cdot CO \cdot CH\colon CH \cdot C_6H_5$, will form additive products with two molecules of mercaptans only.

I have found that this tri-olefinic ketone readily takes up one molecule of either phenyl mercaptan or *iso*amyl mercaptan, and that, on using an excess of phenyl mercaptan, a mixture of compounds con-

taining one and two molecules of the mercaptan is produced. Various attempts to separate this mixture have been unsuccessful.

Like the olefinic ketones, so do the ketones of the acetylene series form additive compounds with mercaptans. These are similar to the substances which are produced from phenylpropiolic and acetylenedicarboxylic esters (see Ruhemann and Stapleton, Trans., 1900, **77**, 1181). As yet I have studied in this connection methoxybenzoylphenylacetylene, $C_6H_5\cdot C\vdots C\cdot CO\cdot C_6H_4\cdot O\cdot CH_3$, which unites with one molecule of phenyl mercaptan. This additive compound differs from the substances which are formed by the union of mercaptans with olefinic ketones inasmuch as it is deep yellow, whilst the latter are almost all colourless.

Analogous to the action of mercaptans on olefinic ketones with the ketonic group in open chains is the behaviour of the mercaptans towards olefinic cyclic ketones. For example, I have used benzylidenephenylmethylpyrazolone, $C_6H_5\cdot N<\begin{matrix}N=C\cdot CH_3\\ \quad\ |\\ CO\cdot C\vdots CH\cdot C_6H_5\end{matrix}$, and the product of the condensation of benzaldehyde with hippuric acid. The latter substance has lately been recognised by Erlenmeyer (*Annalen*, 1904, **337**, 268) as benzylidenephenylazlactone,

$$C_6H_5\cdot C\lessdot\begin{matrix}N-C\vdots CH\cdot C_6H_5\\ \quad\ |\\ CO\cdot O\end{matrix}.$$

Both these compounds readily react with phenyl mercaptan, especially, however, the azlactone, which unites with the mercaptan even without the use of a catalytic agent. Whilst benzylidenephenylmethylpyrazolone takes up one molecule only of the mercaptan, the derivative of azlactone unites with two molecules of the mercaptan. This circumstance, together with the fact that the azlactone ring readily opens, leads to the view that the additive compound of phenyl mercaptan with benzylidenephenylazlactone is probably to be represented thus:

$$C_6H_5\cdot CH_2(S\cdot C_6H_5)\cdot\begin{matrix}C\cdot NH\cdot CO\cdot C_6H_5\\ |\qquad\qquad\\ CO\cdot S\cdot C_6H_5\end{matrix}.$$

EXPERIMENTAL.

iso*Amylthiolbenzylacetophenone*,
$C_6H_5\cdot CH(S\cdot C_5H_{11})\cdot CH_2\cdot CO\cdot C_6H_5$.

The union of benzylideneacetophenone with *iso*amyl mercaptan has been effected by mixing the ketone (2 grams), dissolved in a little benzene, with the mercaptan (1 gram), and adding 3—4 drops of piperidine. After standing overnight, light petroleum is added, when a white solid is precipitated; this is washed with dilute alcohol and crystallised from boiling alcohol, in which it is readily soluble. Thus

colourless prisms are obtained, which melt at 49—50° and dissolve in cold concentrated sulphuric acid, yielding a yellow solution.

0·2019 gave 0·5680 CO_2 and 0·1407 H_2O. C = 76·72; H = 7·74.
$C_{20}H_{24}OS$ requires C = 76·92; H = 7·69 per cent.

Posner (*Ber.*, 1902, **35**, 809), on using hydrogen chloride as catalytic agent, obtained from the ketone and *iso*amyl mercaptan an oily product which he found to be a mixture.

Phenylthiolbenzylacetophenone,
$C_6H_5 \cdot CH(S \cdot C_6H_5) \cdot CH_2 \cdot CO \cdot C_6H_5$.

Benzylideneacetophenone (2 grams), dissolved in cold benzene, interacts with phenyl mercaptan (1·2 grams) on adding a few drops of piperidine, and the reaction is accompanied by development of heat. After a short time, the whole sets to a semi-solid, which dissolves in boiling alcohol with difficulty, and, on cooling, crystallises in colourless needles. These melt at 120—121° and dissolve in cold concentrated sulphuric acid, forming a yellowish-red solution.

0·2010 gave 0·5825 CO_2 and 0·1025 H_2O. C = 79·03; H = 5·66.
$C_{21}H_{18}OS$ requires C = 79·24; H = 5·66 per cent.

This substance is identical with that which Posner (*loc. cit.*) prepared by the action of hydrogen chloride on a mixture of benzylideneacetophenone and phenyl mercaptan. It is formed, also, by the action of phenyl mercaptan on bromobenzylideneacetophenone.

On adding piperidine (3 grams) to the mixture of phenyl mercaptan (2 grams) and bromobenzylideneacetophenone (5 grams), dissolved in alcohol, heat is developed and a solid is formed which crystallises from alcohol in colourless needles. The identity of this compound with phenylthiolbenzylacetophenone has been ascertained by the melting point (121°) and the following analysis:

0·2015 gave 0·5845 CO_2 and 0·1040 H_2O. C = 79·11; H = 5·73.
$C_{21}H_{18}OS$ requires C = 79·24; H = 5·66 per cent

Phenylthiolbenzyldeoxybenzoin,
$C_6H_5 \cdot CH(S \cdot C_6H_5) \cdot CH(C_6H_5) \cdot CO \cdot C_6H_5$.

Posner (*Ber.*, 1904, **37**, 505) previously studied the action of mercaptans on benzylidenedeoxybenzoin, and found that additive products only were formed when the mixture of the ketone and the mercaptan was dissolved in glacial acetic acid and the solutions saturated with hydrogen chloride, the reaction taking place either in the cold or at 40—50°. I find that the union of mercaptans with the olefinic ketone is readily effected by using piperidine as catalytic

agent, and I have examined, especially, the additive product with phenyl mercaptan. This is formed by adding a few drops of piperidine to a mixture of the ketone (2·5 grams), dissolved in warm benzene, and the mercaptan (1 gram). The solution, when cold, deposits a solid which is almost insoluble in alcohol, but dissolves in boiling glacial acetic acid, and, on cooling, crystallises in colourless needles which melt at 204—205°.

0·2000 gave 0·6022 CO_2 and 0·1005 H_2O. C = 82·12 ; H = 5·58.
$C_{27}H_{22}OS$ requires C = 82·23 ; H = 5·58 per cent.

The solution of this substance in concentrated sulphuric acid is yellowish-red.

Ethyl Phenylthiolbenzylbenzoylacetate,
$C_6H_5{\cdot}CH(S{\cdot}C_6H_5){\cdot}CH(CO{\cdot}C_6H_5){\cdot}CO_2{\cdot}C_2H_5$.

Heat is developed on adding 3—4 drops of piperidine to a mixture of ethyl benzoylacetate (2·5 grams), dissolved in benzene, and phenyl mercaptan (1 gram). The solution, which remains clear after being left overnight, is treated with light petroleum, when a white solid is precipitated. This crystallises from alcohol in bunches of colourless needles, which melt at 100—101° and dissolve in cold concentrated sulphuric acid, forming a yellowish-red solution.

0·2013 gave 0·5439 CO_2 and 0·1020 H_2O. C = 73·68 ; H = 5·65.
$C_{24}H_{22}O_3S$ requires C = 73·84 ; H = 5·64 per cent.

Methyl β-Phenylthiol-γ-benzylidenepropyl Ketone,
$C_6H_5{\cdot}CH{:}CH{\cdot}CH(S{\cdot}C_6H_5){\cdot}CH_2{\cdot}CO{\cdot}CH_3$.

Posner (*Ber.*, 1904, **37**, 509), in recording the experiments of his pupil, S. Werner, stated that under the influence of hydrogen chloride mercaptans reacted with cinnamylideneacetone to form oils, which, on oxidation, yielded disulphones. I have not studied the action of potassium permanganate on the substances which are produced by the union of mercaptans with this di-olefinic ketone, because Professor Posner proposes to re-examine the results at which his pupil arrived. I have only ascertained that the behaviour of phenyl mercaptan towards cinnamylideneacetone is analogous to the reaction of mercaptans with cinnamylideneacetophenone, and under the influence of piperidine takes up 1 molecule only of the mercaptan. The ketone (3 grams) dissolves in phenyl mercaptan (2 grams) on slightly warming ; the solution, when treated with a few drops of piperidine, turns red and solidifies after a short time. The solid dissolves in hot light petroleum, and, on cooling, gradually crystallises in colourless prisms, which are readily soluble in alcohol and melt at 53—54°.

0·2009 gave 0·5637 CO_2 and 0·1153 H_2O. C = 76·52; H = 6·40.
0·2015 „ 0·5646 CO_2 „ 0·1162 H_2O. C = 76·41; H = 6·40.
$C_{18}H_{18}OS$ requires C = 76·60; H = 6·38 per cent.,

whilst the additive compound with 2 mols. of the mercaptan, $C_{24}H_{24}OS_2$, requires C = 73·46; H = 6·12 per cent.

The compound dissolves in concentrated sulphuric acid, yielding a deep red solution, as do the additive products of cinnamylideneacetophenone with mercaptans.

The Union of Mercaptans with Cinnamylidenebenzylideneacetone.

The tri-olefinic ketone, $C_6H_5 \cdot CH \colon CH \cdot CH \colon CH \cdot CO \cdot CH \colon CH \cdot C_6H_5$, prepared after Scholtz's directions (*Ber.*, 1896, **29**, 614), readily unites with 1 mol. of phenyl mercaptan, as well as *iso*amyl mercaptan, to form additive products, which may be represented either by the formula $C_6H_5 \cdot CH \colon CH \cdot CH(SR) \cdot CH_2 \cdot CO \cdot CH \colon CH \cdot C_6H_5$ or

$$C_6H_5 \cdot CH \colon CH \cdot CH \colon CH \cdot CO \cdot CH_2 \cdot CH(C_6H_5) \cdot SR$$

(R denoting C_6H_5 or C_5H_{11}).

The additive compound with *iso*amyl mercaptan is best obtained by adding a few drops of an alcoholic solution of sodium ethoxide to the mixture of the tri-olefinic ketone (2·5 grams) dissolved in alcohol and the mercaptan (1 gram). The solid which separates after a short time is very soluble in benzene or chloroform, less so in alcohol, and crystallises from light petroleum in faintly yellow needles which melt at 69—70°.

0·1654 gave 0·4808 CO_2 and 0·1151 H_2O. C = 79·22; H = 7·73.
$C_{24}H_{28}OS$ requires C = 79·12; H = 7·69 per cent.

The solution of this substance in cold concentrated sulphuric acid is magenta-coloured.

The union of phenyl mercaptan with cinnamylidenebenzylideneacetone has been effected by mixing the ketone (2·3 grams), dissolved in benzene, with the mercaptan (1 gram) and adding 4—5 drops of diethylamine. After a few minutes, a solid separates, and in the course of 2 hours the whole mixture sets to a semi-solid. The additive compound is very soluble in chloroform, with difficulty, however, in cold alcohol or benzene, and crystallises from the latter solvent in nearly colourless needles which melt at 133—134°.

0·2030 gave 0·6020 CO_2 and 0·1088 H_2O. C = 80·88; H = 5·95.
$C_{25}H_{22}OS$ requires C = 81·08; H = 5·94 per cent.

The solution of this compound in concentrated sulphuric acid is deep purple.

On using an excess of phenyl mercaptan, I have obtained a product

which melts indefinitely at 127°, and which is a mixture of the ketone with 1 and 2 molecules of the mercaptan. I have tried in vain to separate it by fractional crystallisation, different fractions yielding, on analysis, numbers intermediate between those required for the additive substances with 1 and 2 mols. of the mercaptan.

a-Phenylthiol-β-methoxybenzoylstyrene,
$C_6H_5·C(S·C_6H_5)⁚CH·CO·C_6H_4·O·CH_3$.

Methoxybenzoylphenylacetylene, $C_6H_5·C⁚C·CO·C_6H_4·O·CH_3$, which Stockhausen and Gattermann (*Ber.*, 1892, **25**, 3538) prepared by the action of aluminium chloride on a mixture of phenylpropiolyl chloride and anisole, has since been studied by E. R. Watson (Trans., 1904, **85**, 1324), who showed that it formed additive compounds with various organic bases. Mercaptans also readily unite with the acetylenic ketone, but as yet I have examined only the additive product with phenyl mercaptan. This is formed by mixing the ketone (2 grams), dissolved in benzene, with the mercaptan (1 gram) and adding a few drops of piperidine. Heat is developed, and the yellow solution, which remains almost clear on mixing with light petroleum, yields a solid, which crystallises from alcohol in yellow plates. These melt at 121—122° and dissolve in concentrated sulphuric acid, forming a deep red solution.

0·2005 gave 0·5600 CO_2 and 0·0944 H_2O. C = 76·17 ; H = 5·23.
$C_{22}H_{18}O_2S$ requires C = 76·30 ; H = 5·20 per cent.

4-*Phenylthiolbenzyl*-1-*phenyl*-3-*methylpyrazol*-5-*one*,

$$C_6H_5·N<\begin{matrix}N—C·CH_3\\ \quad | \\ CO·CH(C_6H_5)·S·C_6H_5\end{matrix}.$$

Benzylidenephenylmethylpyrazolone (2·2 grams), when dissolved in benzene, readily reacts with phenyl mercaptan (1 gram) even without the use of a catalytic agent (see Knorr, *Annalen*, 1887, **238**, 179). The deep red colour of the solution rapidly fades, and in the course of a day deposits a white solid; this increases in quantity on adding light petroleum, but at the same time an oil is precipitated which converts the solid into a pasty product. Its solution in hot dilute alcohol, on cooling, yields colourless needles which melt at 140° to a red liquid.

0·2019 gave 0·5490 CO_2 and 0·0993 H_2O. C = 74·15 ; H = 5·46.
0·2168 „ 14·3 c.c. moist nitrogen at 19° and 764 mm. N = 7·62.
$C_{23}H_{20}ON_2S$ requires C = 74·15 ; H = 5·46 ; N = 7·52 per cent.

The solution of this substance in boiling alcohol is red, but on cooling it becomes light yellow; cold concentrated sulphuric acid dissolves the compound, yielding a deep red solution.

Action of Phenyl Mercaptan on Benzylidenephenylazlactone.

The condensation of aldehydes with hippuric acid has been carefully studied by E. Erlenmeyer, jun. For the preparation of the compound which is formed from benzaldehyde and hippuric acid, I have followed his directions (*Annalen*, 1893, **275**, 3), and in examining its behaviour towards phenyl mercaptan I have ascertained that it forms an additive product with 2 mols. of the mercaptan. As has been stated in the introduction to this paper, the compound is probably to be represented thus: $C_6H_5 \cdot CH_2(S \cdot C_6H_5) \cdot C(CO \cdot S \cdot C_6H_5) \cdot NH \cdot CO \cdot C_6H_5$. This substance is obtained by adding a few drops of diethylamine to the mixture of equal weights of benzylidenephenylazlactone and phenyl mercaptan, dissolved in benzene, when after about half an hour the whole sets to a semi-solid mass of crystals. These are sparingly soluble in boiling alcohol, more readily in hot benzene, and on cooling crystallise from the latter solvent in colourless needles which melt at 156—157°.

0·2012 gave 0·5292 CO_2 and 0·0908 H_2O. C = 71·73; H = 5·01.
0·1965 ,, 5·2 c.c. moist nitrogen at 15° and 774 mm. N = 3·15.
$C_{28}H_{23}O_2NS_2$ requires C = 71·64; H = 4·90; N = 2·99 per cent.

The additive compound dissolves in cold concentrated sulphuric acid, yielding a yellow solution which gradually darkens and finally becomes deep red.

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LVIII.—*The Tautomerism of Acetyl Thiocyanate.*

By Augustus Edward Dixon and John Hawthorne.

It is now fairly well established that, among the products resulting from the interaction of metallic thiocyanates with various organic acid chlorides, there is so far not one which, if placed under suitable conditions, cannot behave as thiocarbimide.

On the other hand, it is doubtful if any acid thiocarbimide has yet been produced from which it is impossible to obtain indications of thiocyanic character (see Trans., 1904, **85**, 807). In a few cases, no doubt, for example, that of benzoylthiocarbimide, PhCO·NCS, the characters are, for all practical purposes, entirely thiocarbimidic, the substance, which is moderately easily decomposed by contact with water, yielding thereby no thiocyanic acid (Miquel, *Ann. Chim. Phys.*, 1877, [v], **11**, 302), but carbon oxysulphide instead. Never-

theless, even from this well-defined compound, Wheeler (*Amer. Chem. J.*, 1901, **26**, 349), by treating the alcoholic solution with sodium, has succeeded in obtaining the reaction for a thiocyanate, and he records experiments by T. B. Johnson, from which it appears that, when caused to interact with ethyl sodiomalonate, sodium formanilide, and other sodium derivatives, the NCS group is withdrawn as sodium thiocyanate. That treatment so severe as this is necessary to develop its thiocyanic character is evidence showing how feebly the latter is retained: it may be added that, so far as is known at present, this pronounced tendency to exert thiocarbimidic functions is mainly, if not entirely, confined among derivatives of the form R·CO·NCS, to those in which the hydrocarbon radicle, R, is benzenoid in nature. If R is aliphatic, the ability of the combined NCS group to unite directly with various kinds of other molecules to form additive compounds is often greatly weakened, and in certain interactions is practically lost, the sulphuretted group now entering into double decompositions whereby thiocyanic acid is formed, together with a substituted amide.

In some cases, the behaviour of the CNS group appears to depend almost entirely on what material is allowed to interact with it: thus, stearyl thiocyanate gave with benzylaniline (Trans., 1896, **69**, 1602) more than 95 per cent. of the theoretical yield of stearylphenylbenzylthiourea (supposing it to be purely thiocarbimidic), and with other bases yields of 90 per cent. and upwards; but with ammonia it gave practically nothing save thiocyanic acid and stearamide.

For want of a better term the power whereby these acidic derivatives yield such variable products has been called "tautomeric" in earlier papers, but it may be doubted whether the word "tautomerism," even if taken in a wide sense, can properly be made to include the phenomena mentioned above. As used by van Laar (*Ber.*, 1885, **18**, 648), it implied the migration, or rapid oscillation, of a relatively light atom in the molecule, the configuration of which thus became temporarily modified; such a movement about the SCN nucleus, however, can scarcely be postulated, consistently with stable equilibrium, for a group like stearyl, considering that the former is nearly five times as heavy as the latter.

But if the radicle of the acid cannot be supposed to move round the CNS group, it is difficult to understand how this may exhibit alternative behaviour as -NCS or as -SCN, unless on the hypothesis that this whole atomic complex itself can oscillate in such a way as to present either the nitrogen or the sulphur to the carbon of the carbonyl group. And if such an oscillation is suggested to

explain the observed results, the process may perhaps be designated "tautomeric" in so far as it implies a temporary displacement of parts within a molecule, otherwise unchanged, but it no longer includes the notion of something very light as compared with the whole mass, the mobility of which from point to point, without disturbing or destroying the general equilibrium, is dependent on that relative lightness.

Before proceeding to account for the phenomena referred to by inventing still another kind of intramolecular movement, it is reasonable to inquire whether the results, as well as others which have recently been observed, cannot be explained in terms of hypotheses already existing.

Two forms of isomerism are well known which seem, at first sight, to present more or less similarity to that now under consideration; they are (i) that of the nitrites with the nitro-compounds, and (ii) that subsisting between the *iso*cyanides and the nitriles. Beyond the fact, however, that in class (i) a given metallic nitrite is able to produce both forms simultaneously, there appears to be little in common between this isomerism and that of the thiocarbimides and thiocyanates, and it is not further considered here.

On the other hand, the isomerism of the cyanides and *iso*cyanides presents, superficially at least, a good deal of resemblance to that of the thiocyanates and *iso*thiocyanates; the nature of this analogy is indicated below.

(i) Metallic cyanides, by interaction with organic haloids, yield sometimes nitriles, sometimes *iso*cyanides, and frequently both together; metallic thiocyanates give rise to thiocarbimides or to thiocyanates, and occasionally, it would seem, to mixtures of both.

(ii) *iso*Cyanides show some tendency to pass, at high temperature, into the isomeric normal cyanides; in like manner, the hydrocarbon thiocyanates are sometimes convertible into thiocarbimides.

(iii) The above change (ii), when once definitely effected, appears to be permanent.

(iv) The tendency of nitriles is to change principally through the addition of molecules, whereas the *iso*cyanides tend during interaction to decompose; with thiocarbimides and thiocyanates, respectively, the like is true, as a general rule.

(v) Pure nitriles are reputed to have a not unpleasant odour, whilst the *iso*cyanides are very foul-smelling; the odour of thiocarbimides is sharp, but not disagreeable, whilst the isomeric thiocyanates have often a very offensive, garlic-like smell.

There are a good many other points of resemblance, besides those set forth in the foregoing list, but the analogy is not perfect in every detail, and must not be pressed too far; the boiling points,

for instance, of the nitriles lie above those of the *iso*cyanides, whereas the thiocarbimides boil at lower temperatures than the isomeric thiocyanates.

Our knowledge of the relations subsisting between the normal and *iso* cyanogen compounds has been summed up by J. Wade in a paper on the constitution of the metallic cyanides (Trans., 1902, **81**, 1596), wherein he shows that the production of nitrile, as well as *iso*cyanide, during the interaction between metallic cyanides and organic haloids cannot adequately be explained, either by the hypothesis of isomeric conversion (of initially formed *iso*cyanide into nitrile) or by the hypothesis of tautomerism, in van Laar's sense, of the metallic cyanide used, but is intelligible on the supposition that additive compounds are first formed from a metallic *iso*cyanide, and are subsequently decomposed. In this way, the production of propionitrile from potassium *iso*cyanide can be explained:

(i) K·N⁚C + EtI = K·N⁚CIEt.
(ii) K·N⁚CIEt = KI + N⁚CEt.

In this paper he conjectures also that the additive hypothesis might serve to explain the production of methyl *iso*cyanate from silver cyanate without its being necessary to suppose that the silver is in direct union with the nitrogen:

AgO·CN + MeI = AgO·CI⁚NMe = AgI + O⁚C⁚NMe.

However this may be as regards oxygen compounds, it can scarcely explain the formation of the corresponding sulphur derivatives, for amongst saturated hydrocarbon haloids it is very rarely that a thiocarbimide is produced by interaction with a metallic thiocyanate, and in the case of unsaturated alkylogens the change from a thiocyanate, first formed, into a thiocarbimide can easily be followed. Wheeler, in fact, has gone so far as to lay down the principle, that in no case is a true thiocarbimide initially produced by interaction with a metallic thiocyanate, but that, when one does appear, it originates indirectly through the isomeric rearrangement of the corresponding thiocyanate.

In the case of acidic derivatives, namely, those containing the group R·CO, or the group R·O·CO, it is different, because, as mentioned earlier, the product of the interaction invariably has the power to behave as thiocarbimide. This power, it may here be noted, is not one which grows on keeping, or is developed by heat; it is manifested at once, as soon as any interaction has taken place, and can occasionally be observed in solutions which have never been warmed, or allowed to become warm through interaction (compare Doran, Trans., 1901, **79**, 907). So far as concerns the products

derivable from aliphatic acids, the additive hypothesis will not cover all the facts necessary for CNS combinations, because it does not explain why a given compound of this class, when already prepared, may act with one base as R·CO·NCS, and with another as R·CO·SCN.

From the fact just mentioned, it seems reasonable to conclude that the differences in behaviour of such acidic "thiocarbimides" or "thiocyanates" are conditioned neither by isomeric conversion of a substance initially formed nor by ordinary tautomerism (even if such were admissible) of the parent metallic salt; neither can the additive hypothesis explain variability of function in its own product. There seems, in fact, to be no escape from the view, already propounded definitely by one of us (Trans., 1901, **79**, 541), that there may exist in the so-called "thiocyanates" of certain electro-negative radicles the capacity to behave either as such or as thiocarbimides, according to the conditions under which they are caused to interact.

Whether this alternative behaviour of the CNS group is potential in the group itself, or whether the power to assume one or other form is somehow conditioned by the chemical nature of the other substance presented for interaction, was still uncertain, when a chance observation, made in this laboratory by the late R. E. Doran, led to the discovery that, in one interaction at least, the power of the sulphuretted acidic compound to act as thiocarbimide or as thiocyanate is, for all practical purposes, dependent neither on the contained sulphur radicle nor on the chemical nature of the molecule presented to it, but is simply a function of the temperature at which interaction is caused to occur. The particular case referred to is that where Miquel's "acetyl thiocyanate" and aniline are mixed together in presence of dry benzene: if the mixture is made at the boiling point of the solutions, the constituents unite, in the main, to form acetylphenylthiocarbamide,

$$CH_3{\cdot}CO{\cdot}NCS + C_6H_5{\cdot}NH_2 = CH_3{\cdot}CO{\cdot}NH{\cdot}CS{\cdot}NH{\cdot}C_6H_5,$$

whereas, if they are brought into contact near the freezing point of water but little thiocarbamide is formed, the materials undergoing instead a double decomposition, thus:

$$CH_3{\cdot}CO{\cdot}SCN + C_6H_5{\cdot}NH_2 = CH_3{\cdot}CO{\cdot}NH{\cdot}C_6H_5 + H{\cdot}SCN.$$

A paper setting forth these results, and describing briefly the methods whereby they were attained, has recently been published (Trans., 1905, **87**, 331). Unhappily, the work had scarcely passed the stage of mere preliminary experiment, when it was terminated by Doran's early death.

As the experimental methods adopted in these preliminary trials

were capable of affording only very rough approximations to the actual values, we have undertaken to pursue the study further, with especial reference to the more precise determination of the weights of thiocarbamide and of thiocyanic acid produced, and to the maintenance of more uniform temperatures during the interactions. So far, we have examined only the aniline-acetyl-"thiocyanate" system.

Experimental.

The acetyl thiocyanate was usually prepared by warming on the water-bath, in a reflux apparatus, a mixture of pure acetyl chloride, excess of lead thiocyanate, and benzene, toluene, or xylene, carefully dried over sodium; when interaction was complete, the liquor was filtered off at the pump and used without delay, because the product soon changes, becoming reddish-brown, and, later on, dark and turbid. In some cases, the thiocyanate itself was first isolated according to Miquel's directions (*loc. cit.*), further purified by one or more rectifications, and then diluted with one of the above-mentioned solvents: no difference of any account was observed in the results when using such material, except that somewhat larger total yields were obtained than where the first process was employed, the deficiency, when starting from acetyl chloride, arising probably through a slight loss of this substance by volatilisation. Incidentally, it may be noted that the boiling point of acetyl thiocyanate lies slightly above the temperature (132—133°) given by Miquel, a sample thrice distilled boiling at about 134·5°.

The aniline used was prepared from the sulphate, and when freed from water and redistilled, the boiling point of a litre varied by less than 1° throughout the distillation.

In each experiment, whether ready-formed acetyl thiocyanate was employed or that prepared in solution from the chloride, the amount taken was always about 5·05 grams, and the volume of solvent was kept approximately constant, being about 50 to 80 c.c., except in a few cases at low temperature, where the bulk was increased. When operating at medium temperatures, the process was conducted by charging a stoppered burette with a mixture of 9·3 grams (2 mols.) of aniline with 10 c.c. of solvent, and dropping the liquid slowly into the solution of the thiocyanate, contained in a flask, surrounded by water at the required temperature, and kept constantly in motion, with a view to preclude local accumulation of the base. A thermometer with small bulb was immersed in the contents of the flask, and the rate of introduction of the aniline was so regulated that the variation of temperature of the reagents rarely exceeded 1°. Any considerable excess of aniline was found to render the products oily and difficult to handle; therefore its

admission was stopped when the free base could be detected in the solution.

At low temperatures, the water-bath is replaced by a suitable cooling mixture, and the aniline solution is run in from a pipette, the bulb of which is immersed in ice and salt. Combination occurs vigorously, with development of much heat, so that caution is necessary in mixing: forty-five minutes is little enough to allow for the saturation of 5 grams of thiocyanate, and the base must be added uniformly, as well as slowly, for otherwise the heat evolved locally may bring about very inaccurate results—in fact, a number of our earlier experiments, made before the necessity for slowness in working had been appreciated, were so discordant as to be worthless.

At the higher temperatures, from 70° upwards, the danger from local overheating becomes less marked, since the products tend to remain dissolved in the hot liquid, instead of separating out as a paste; but other difficulties now arise. In the first place, the rate of change of function of acetyl thiocyanate becomes much more rapid, so that a comparatively small error in the maintenance of the temperature of interaction exerts a relatively great influence on the proportions of the products: in the second place, hydrogen sulphide is evolved, thereby withdrawing a portion of the sulphur from the system; and thirdly, aniline thiocyanate tends at high temperatures to undergo isomeric change into phenylthiourea. Of these difficulties the first can obviously be met by precision in the establishment of the temperature, but unfortunately this cannot well be secured in most cases, save by compelling gradual interaction, and slowness is a condition incompatible with the avoidance of the other troubles. As it seemed most important to avoid the loss of essential material, or the conversion of one of the two substances, the proportions of which were under measurement, into the other (thiocyanate into thiocarbamide), we have worked as quickly as possible at the highest temperatures, rapidly cooling the products as soon as the mixture was completed; in these circumstances, no considerable loss of hydrogen sulphide occurs, and the amount of isomeric change undergone by aniline thiocyanate in the course of a few seconds (or even of minutes) is probably of small account. But in such cases, the measurement of temperature was not exact to within a few degrees.

At the highest temperatures, a clear liquid results, from which, as it cools, a crystalline mass is deposited; at low temperatures, a precipitate forms at once, which either is solid, or else solidifies during the slow course of the interaction. When working at intermediate temperatures—say from 10° to 70°—an oil separates, even

although all the materials are very carefully dried; but in such cases, if the mixture is cooled and shaken for a while, the oil presently granulates, and then can be dealt with easily. An equal volume (but not more) of light petroleum is slowly added, and the mixture allowed to remain, preferably for not less than an hour, without access of moisture; then the liquor is drawn off at the pump, the residue washed with a mixture of benzene and light petroleum in equal volumes, and finally with light petroleum alone. The main residue is powdered, dried for many hours at a gentle heat, and weighed: the liquor, when evaporated at the atmospheric temperature, leaves a trifling amount of solid, together, perhaps, with a little aniline; the latter can be removed by treatment with a few c.c. of the benzene-ligroin mixture and subsequent washing with ligroin. The weight of solid thus obtained is generally insignificant, amounting to one- or two-tenths of a gram in 100 c.c. of liquor.

Analysis of the Products.—By the method just described the products were resolved into two parts, (i) the material which separated, and (ii) the soluble portion recovered from the mixture of hydrocarbon solvents. Of the total weight obtained, the former constituted, on the average, about 97 per cent., and consisted of acetylphenylthiocarbamide, together with aniline thiocyanate and acetanilide; the latter contained thiocarbamide and anilide, but no measurable amount of thiocyanate.

After drying the main crop to a constant weight, the whole was ground up with water and washed on a filter with successive quantities of cold water, until the washings ceased to give any red coloration with ferric chloride; the filtrate was then made up to 250 c.c., further diluted, if necessary, to one-eighth of the original strength, and the contained thiocyanic acid determined by Barnes and Liddle's method, using sodium hydrogen sulphite and standard copper sulphate, with potassium ferrocyanide as indicator. The weight of aniline thiocyanate was calculated as a percentage of the joint total yield, and, since the amount of acetanilide formed is conditioned by that of the aniline salt, the sum of the two was calculated also as a percentage of the total product.

In well conducted experiments, the residue after extraction by water was pure white, or nearly so; it was collected, dried by prolonged gentle heating, and weighed: it could consist either of acetanilide alone, of acetylphenylthiocarbamide, or of a mixture of both.

As a means of determining the proportion of thiocarbamide present, a weighed quantity of this residue in alcoholic solution was boiled with excess of $N/10$ silver nitrate in presence of

ammonia, the precipitated sulphide filtered off, and the amount of residual silver measured by Volhardt's method, using standard ammonium thiocyanate. Test experiments, made with pure acetylphenylthiocarbamide, gave sharply quantitative numbers, and on repeating with a mixture of this substance with its own weight of pure acetanilide, the method proved equally satisfactory, and was therefore adopted.

Acetylphenylthiocarbamide is not quite insoluble in water, and hence a little passed into solution in the water used for extracting the aniline thiocyanate; its amount was determined by precipitating a known bulk of the solution, heated previously to boiling, with ammonia and silver nitrate, and treating the precipitate alternately with boiling water and warm ammonia until silver sulphide alone was left; the residue was then dried, weighed, and calculated as acetylphenylthiocarbamide. Another method, adopted in cases where the quantity of thiocyanate was small, consisted in treating the solution with excess of standard silver nitrate in presence of ammonia, acidifying with dilute nitric acid, filtering, and determining the residual silver nitrate; by deducting from the total silver absorbed, that required to form thiocyanate, the difference indicated the thiocarbamide. Naturally, the quantity of dissolved thiocarbamide varied somewhat in different extracts, the highest and the lowest of half a dozen determinations being 0·2 and 0·08 respectively, and the average about 0·14 gram: the number being so small, compared with the total amount of products, it was not considered necessary to measure it in every case.

From the hydrocarbon solvents, after evaporation and removal of the surplus aniline, little was obtained, the precipitation, if the time of standing with light petroleum was not too short, being nearly complete. On the average, less than 0·4 gram was recovered from the solvents, and of this residue, one-fourth, or thereabouts, consisted of thiourea, the amount of which was determined either by the production of silver sulphide or else by the direct volumetric method described above. Practically, it may be reckoned that nearly 0·1 gram of acetylphenylthiocarbamide remains dissolved in each 100 c.c. of solvents: in most of our experiments, this would represent less than one per cent. of the total weight of products obtained.

Since the preparations were conducted under nearly uniform conditions, save, of course, as regards temperature (and occasionally, the degree of dilution), and the method of working has already been set forth in general terms, it is unnecessary to describe the experiments in detail. The results are summarised in the following table, which shows, for each temperature:

(i) The total quantity of acetylphenylthiocarbamide found by analysis, namely, that in the main product after removal, by treatment with water, of the admixed aniline thiocyanate; that in the aqueous extract; and that obtained from the hydrocarbon solvents.

(ii) The weight of aniline thiocyanate, determined by the process of Barnes and Liddle, contained in the aqueous extract.

(iii) The weight of acetanilide calculated from (ii), on the principle that, for each mol. of thiocyanic acid found, one mol. of acetanilide is present:

$$Ac{\cdot}SCN + PhNH_2 = HSCN + Ac{\cdot}NHPh.$$

(iv) The sum of the above weights, and

(v) The total weight of mixed products actually obtained.

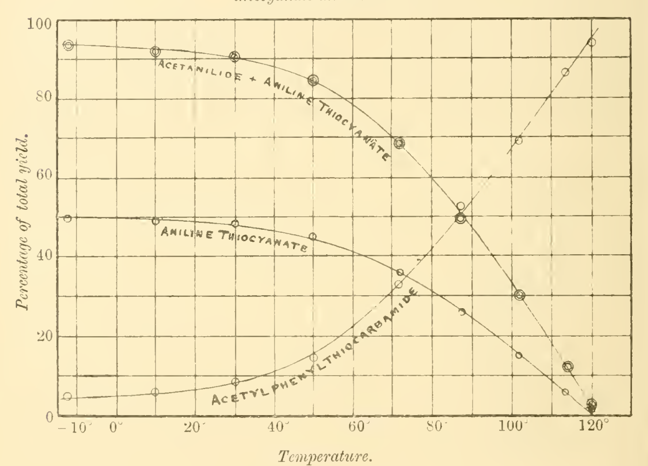
Nos. (vi), (vii), (viii) show the relative amounts of acetylphenylthiocarbamide, aniline thiocyanate, and aniline thiocyanate + acetanilide respectively; these numbers are calculated, each as a percentage of (v), that is, of the total quantity of mixed products determined by direct weighing.

Temperature ...	−12°.	10°.	30°.	50°.	72°.	87°.	102°.	114°.	Above 114°.
(i) Weight of CSN_2H_2AcPh ...	0·58	0·70	0·92	1·57	3·64	5·30	7·04	7·20	8·01
(ii) Weight of $PhNH_2,HSCN$...	6·38	5·27	5·24	4·87	3·97	2·60	1·62	0·51	0·11
(iii) Weight of AcNHPh calculated from (ii) ...	5·66	4·68	4·66	4·33	3·53	2·30	1·44	0·45	0·10
(iv) Sum of the above weights	12·62	10·65	10·82	10·77	11·14	10·20	10·10	8·16	8·22
(v) Total products by direct weighing..	12·81	10·81	10·88	10·82	11·03	10·00	10·21	8·32	8·48
(vi) CSN_2H_2AcPh per cent.	4·5	6·5	8·5	14·5	33·0	53·0	69·0	86·5	94·5
(vii) $PhN_2,HSCN$ per cent.	49·8	48·8	48·2	45·0	36·0	26·0	15·0	6·1	1·3
(viii) $PhNH_2,HSCN$ + AcNHPh per cent.	94·0	92·0	91·0	85·0	68·0	49·0	30·0	11·5	2·5

Considering the rather small scale on which these experiments were conducted, no very great precision could be looked for in the results, which, in fact, sometimes differed from one another in duplicate experiments at a given temperature by several units per cent.; where any material discrepancy arose, the process was repeated (occasionally three or four times), and the mean taken of the most concordant numbers. By increasing the weight of thiocyanate employed for each measurement to 15 or 20 grams, results could probably be obtained which were accurate to within one per cent., provided that the duration of mixing was proportionately extended—say, to four or five hours at any temperature below 50°. At low temperatures the process is very sensitive, and if the rate of mixing

is hurried or irregular, the proportion of thiocarbamide formed at about 0° may increase to 10 per cent. or even higher, with, of course, a corresponding diminution in the proportion of thiocyanate. Sometimes, although rarely, notwithstanding that every care seems to have been used, perplexing irregularities occur; for example, in one experiment, conducted with a pure sample of acetyl thiocyanate at −12°, a thermometer immersed in the pasty mixture showed a variation of 2° at most, yet the yield of aniline thiocyanate + acetanilide reached only 87·5 per cent.—that is, some seven or eight units below the normal amount.

Curve showing the influence of temperature on the interaction between acetyl thiocyanate and aniline.



According to our experience, the method employed for the determination of thiocyanic acid is not quite accurate; whatever error arises in the measurement of the thiocyanic acid is increased by nearly five times when this is calculated to aniline thiocyanate + acetanilide: the sum could amount to fully 2 per cent. We always made two or more determinations so as to reduce this error.

In the accompanying curve, against the temperature (abscissæ) are plotted as ordinates the yields, reckoned as percentages of the total product, of (i) acetylphenylthiocarbamide, (ii) the aniline thiocyanate, (iii) the latter, together with the corresponding (calculated) amount of acetanilide. Curves (i) and (iii) are practically identical in shape, and cut one another at about 87°, at which temperature

the amounts of both thiocarbamide and of acetanilide + thiocyanate are the same, namely, 50 per cent. It should be added that in the case where the percentage yields are plotted against 120° on the curve, the temperature was not measured: these numbers represent the results of a single experiment made with a specimen of pure distilled acetyl thiocyanate in commercial xylene at a temperature near the boiling point of the mixture. Although the sum of the acetanilide and aniline thiocyanate was only 2½ per cent. of the total, the acetylphenylthiocarbamide found did not reach the expected amount, namely, 97½ per cent., the number obtained being only 94½ per cent.

It will be noticed that at the highest temperatures the total amount of the three products, as determined by analysis and referred to the total weight of material actually collected, falls somewhat short of 100 per cent.; this may be explained partly by the fact that a little hydrogen sulphide escapes, and partly through the production of a small quantity of phenylthiourea; the bitter taste of this substance could be detected in the residues, after extraction by water, of preparations made at 100° and upwards.

The maximum amount of aniline thiocyanate obtained in any experiment was 50 per cent.; if no thiocarbamide whatever were formed, but the SCN group produced aniline thiocyanate quantitatively, the corresponding number would be 53 per cent. In some of our experiments, the residue after extraction by water contained no measurable amount of acetylphenylthiocarbamide, the traces formed being distributed between the aqueous extract and the hydrocarbon solvents, but in no case was it entirely absent.

One experiment, made to test a special point, requires individual mention. Acetyl thiocyanate, while undergoing distillation under the ordinary pressure, is subjected to a somewhat high temperature (134—135°), a condition which might dispose it towards isomeric rearrangement into the corresponding thiocarbimide. That such change does not occur, at least to any material extent, is evident from the facts that the boiling point undergoes no change by repeated distillation of the substance, and that the distillate, if treated with well-cooled aniline, yields a product containing less than one-twentieth of its weight of acetylphenylthiocarbamide. It seemed possible, however, that the rate of conversion of thiocyanate into thiocarbimide might be so slow that little of this would be formed during the short time occupied by a distillation; whilst, on the other hand, the prolonged operation of mixing with aniline might afford sufficient time for the isomeride to be produced. If so, aniline thiocyanate would be formed at first and the acetylphenylthiocarbamide later on, and if the rate of isomeric change increased

with the temperature, the observed phenomena would be explained. Such a hypothesis does not harmonise very well with the fact that acetylphenylthiocarbamide is produced abundantly at high temperatures, even when the time of interaction is reduced to a few seconds; but these quickly conducted experiments (in boiling toluene, &c.) were not performed until near the end of the series, and meanwhile the validity of the above conjecture was tested directly, as follows.

One preparation was effected in the usual way at 50°, the products being carefully measured; another experiment was now carried out, using a portion of the same sample of acetyl thiocyanate, and parallel in every respect, save that, before treatment with aniline, the acetyl compound was kept for two hours at the temperature of interaction, namely, 50°. Since the process of mixing occupied nearly three-quarters of an hour in each case, the entire duration of heating in the latter was, roughly, four times that of the former, and consequently, if isomeric change were occurring gradually under the influence of heat, the total yields must be different, and the like must hold for the relative proportions of thiocyanate and of thiocarbamide.

This, however, was not the case: the total yields in both cases were practically the same (10·85 and 10·87 grams, respectively); the percentages of contained thiocyanate were identical (44), whilst the percentage of acetylphenylthiocarbamide in the second experiment, instead of being increased, was somewhat less than in the first. From these and the other experiments mentioned, we conclude that the change of function conditioned by change of temperature in acetyl thiocyanate when this interacts with aniline is not of that permanent character which is implied by the term "isomeric," but is purely temporary, varying from degree to degree according to the temperature. At each given temperature within wide limits, the interaction runs a definite course, which appears to be determined solely by the existing temperature, and independent of previous heating or cooling of the thiocyanate.

It would be premature at this early stage to advance a definite opinion as to the cause of this phenomenon: in one way, it presents a certain analogy to dissociation, save that here, instead of a compound breaking to a greater or less extent, for the time being, into separate groups, a kind of polarisation may be conceived to occur, in which, with rising temperature, the sulphur atom of the SCN nucleus tends to move away from the acetyl residue, and the nitrogen simultaneously to swing round towards it, but without becoming permanently associated, as in the case of the hydrocarbon

thiocarbimides, and other members of the true thiocarbimidic class.

The outcome of the present investigation, in so far as it goes to prove that Miquel's acetyl thiocyanate, when interacting with aniline, behaves at low temperatures mainly as thiocyanate and at high temperatures principally as thiocarbimide, serves to confirm the work of Doran, already mentioned. But as regards the experimental data on which the general conclusion is based in each case, there is little similarity; neither, indeed, do the results admit of comparison, since the methods of measurement differed essentially. It seems probable that the discrepancies between his numbers and our own were due, to some extent, to his having relied exclusively, for the quantitative separation of the products, on the solvent power of water and of diluted alcohol, a method which we found unsuitable for the purpose. Moreover, in his experiments, great variations of temperature were permitted to occur, whilst, as already stated, we were unable to obtain concordant data, save by most rigid control of the temperature and by checking our results by duplicate experiments.

There is reason to believe that the variability of function of acetyl thiocyanate and of certain other thiocyanates with respect to their interaction with bases is not limited to the case where aniline is employed, and it is proposed to extend the present inquiry, in the hope that further examples of this variety of tautomerism may be forthcoming, and with a view to learn more about its nature.

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LIX.—*The Chemical Dynamics of the Reactions between Sodium Thiosulphate and Organic Halogen Compounds. Part II. Halogen-substituted Acetates.*

By Arthur Slator, Ph.D.

In a previous publication (Trans., 1904, 85, 1286) it has been shown that sodium thiosulphate reacts readily with certain organic halogen compounds, and that the reactions proceed with a measurable velocity. The action of sodium thiosulphate on the methyl, ethyl, and ethylene haloids is in most cases a bimolecular change, the velocity of the reaction being proportional to the concentration of the halogen

compound and to that of the thiosulphate. The investigation of such changes has been extended, and in the present communication an account is given of the reactions between sodium thiosulphate and the following substituted acetates:

$CH_2I{\cdot}CO_2{\cdot}C_2H_5$	$CH_2Br{\cdot}CO_2{\cdot}C_2H_5$	$CH_2Cl{\cdot}CO_2{\cdot}C_2H_5$
	$CH_2Br{\cdot}CO_2{\cdot}CH_3$	$CH_2Cl{\cdot}CO_2{\cdot}CH_3$
	$CH_2Br{\cdot}CO_2Na$	$CH_2Cl{\cdot}CO_2Na$.

These acetates react, forming the compound where the halogen is replaced by the group NaS_2O_3, thus:

$$CH_2Br{\cdot}CO_2{\cdot}C_2H_5 + Na_2S_2O_3 = NaS_2O_3{\cdot}CH_2{\cdot}CO_2{\cdot}C_2H_5 + NaBr.$$

The derivatives can easily be isolated, and have already been investigated by Purgotti (*Gazzetta*, 1892, 22, 416).

The velocity of these reactions has been measured by the method described in the previous paper (*loc. cit.*). The remarkable reactivity of these compounds renders it possible to make the measurements in very dilute solution and at a low temperature. The evaporation of the esters from these aqueous solutions is negligible, and the reaction can therefore be carried out in flasks. Such measurements show the changes to be in all cases bimolecular, and undisturbed by subsidiary reactions.

The velocities of the reactions between ethyl bromoacetate and the following thiosulphates have also been measured:

$K_2S_2O_3$	BaS_2O_3	$Na_3Ag(S_2O_3)_2$	$Na_2Pb(S_2O_3)_2$
$(NH_4)_2S_2O_3$	SrS_2O_3		PbS_2O_3.

The results obtained show that the reaction-velocity is probably strictly proportional to the S_2O_3'' ion, and that the undissociated and partially dissociated NaS_2O_3' ions have no direct action.

The velocities of other reactions in which the halogen-substituted acetates take part have been measured by other investigators, but only two of them involve the replacement of the halogen.

Schwab has investigated the hydrolysis of sodium chloroacetate to sodium glycollate by the action of caustic soda (van't Hoff, "Studies in Chemical Dynamics," p. 15), and Buchanan has measured the rate of transformation of chloroacetic acid into glycollic acid by the action of water (van't Hoff, *ibid.*, p. 14). These reactions were measured at a temperature of 100°, and proceed much more slowly than those described in this paper.

Experimental.

Ethyl iodoacetate, ethyl bromoacetate, and methyl bromoacetate interact at 25° with one equivalent of sodium thiosulphate:

0·0982 gram $C_4H_7O_2I$ required 46·5 c.c. $N/100$ $Na_2S_2O_3$ = $C_4H_7O_2I : 1·01\ Na_2S_2O_3$.
0·0680 gram $C_4H_7O_2I$ required 31·9 c.c. $N/100$ $Na_2S_2O_3$ = $C_4H_7O_2I : 1·00\ Na_2S_2O_3$.
0·1066 gram $C_4H_7O_2Br$ required 62·8 c.c. $N/100$ $Na_2S_2O_3$ = $C_4H_7O_2Br : 0·98\ Na_2S_2O_3$.
0·1040 gram $C_4H_7O_2Br$ required 60·8 c.c. $N/100$ $Na_2S_2O_3$ = $C_4H_7O_2Br : 0·98\ Na_2S_2O_3$.
0·1052 gram $C_3H_5O_2Br$ required 69·6 c.c. $N/100$ $Na_2S_2O_3$ = $C_3H_5O_2Br : 1·01\ Na_2S_2O_3$.
0·1206 gram $C_3H_5O_2Br$ required 78·6 c.c. $N/100$ $Na_2S_2O_3$ = $C_3H_5O_2Br : 1·00\ Na_2S_2O_3$.

The velocities of these reactions are very great, and measurements were therefore carried out in very dilute solution ($N/200$—$N/100$) and large quantities (25—50 c.c.) of the reaction-mixture were titrated. The reactions are bimolecular, and the temperature quotient is in each case about 2·8. In the following tables the notation is the same as that employed in the previous paper (Trans., 1904, **85**, 1291).

Table I.—*Ethyl Iodoacetate.*

Temperature 25°. 50 c.c. titrated. I = 0·0111 N.

Time.	($Na_2S_2O_3$).	($C_4H_7O_2I$).	$K \times C_\infty$.
0	22·8	21·0	—
5	16·6	14·8	0·00282
10	13·1	11·3	0·00285
20	9·4	7·6	0·00283
35	6·8	5·0	0·00279
50	5·3	3·5	0·00288
∞	1·8	0·0	—
		Mean............	0·00283

K = 7·1
Other expts. gave K = 6·9
K = 7·0
Mean......... 7·0

Temperature 15°. 25 c.c. titrated. I = 0·0111 N.

Time.	($Na_2S_2O_3$).	($C_4H_7O_2I$).	$K \times C_\infty$.
0	19·6	16·7	—
5	16·2	13·3	0·00320
15	12·2	9·3	0·00322
30	9·05	6·15	0·00327
50	6·95	4·05	0·00330
∞	2·9	0·0	—
		Mean............	0·00325

K = 2·52
Other expts. gave K = 2·52
K = 2·61
Mean......... 2·55

Temperature quotient = 2·75.

TABLE II.—*Ethyl Bromoacetate.*

Temperature 25°.

50 c.c. titrated. I = 0·0110 N.

Time.	($Na_2S_2O_3$).	($C_4H_7O_2Br$).	$K \times C_\infty$.
0	37·25	32·85	—
5	24·7	20·3	0·0061
10	18·75	14·35	0·0062
15	15·3	10·9	0·0062
25	11·6	7·2	0·0061
40	8·85	4·45	0·0061
∞	4·4	0·0	—
		Mean............	0·0061

$K = 6·3$
Other expts. gave $K = 6·2$
$K = 6·6$

Mean......... 6·4

Temperature 15°.

25 c.c. titrated. I = 0·0110 N.

Time.	($Na_2S_2O_3$).	($C_4H_7O_2Br$).	$K \times C_\infty$.
0	20·45	25·45	—
5	15·6	20·6	0·0052
10	12·45	17·45	0·0052
20	8·6	13·6	0·0052
35	5·6	10·6	0·0052
58	3·4	8·4	0·0051
∞	0·0	5·0	—
		Mean............	0·0052

$K = 2·36$
Duplicate expt. $K = 2·36$

Mean......... 2·36

Temperature quotient = 2·75.

TABLE III.—*Methyl Bromoacetate.*

Temperature 25°.

50 c.c. titrated. I = 0·0110 N.

Time.	($Na_2S_2O_3$).	($C_3H_5O_2Br$).	$K \times C_\infty$.
0	30·3	24·45	—
5	22·5	16·65	0·0075
10	18·15	12·3	0·0076
20	13·6	7·75	0·0076
30	11·25	5·4	0·0075
50	8·9	3·05	0·0074
∞	5·85	0·0	—
		Mean............	0·0075

$K = 5·85$
Duplicate expt. $K = 5·8$

Mean......... 5·85

Temperature 15°.

25 c.c. titrated. I = 0·0110 N.

Time.	($Na_2S_2O_3$).	($C_3H_5O_2Br$).	$K \times C_\infty$.
0	23·3	22·3	—
5	18·9	17·9	0·00091
10	15·9	14·9	0·00092
20	12·15	11·15	0·00091
30	9·9	8·9	0·00090
40	8·35	7·35	0·00091
60	6·5	5·5	0·00089
∞	1·0	0·0	—
		Mean............	0·00091

$K = 2·09$
Duplicate expt. $K = 2·08$

Mean......... 2·09

Temperature quotient = 2·8.

Experiments in which pure bromoacetic acid was weighed out, neutralised with sodium hydroxide, and allowed to interact at 25° with excess of sodium thiosulphate show that these salts react in equivalent proportions.

0·0190 gram $C_2H_3O_2Br$ required 13·7 c.c. $N/100$ $Na_2S_2O_3$ = $C_2H_3O_2Br : 1·00\ Na_2S_2O_3$.

0·0493 gram $C_2H_3O_2Br$ required 34·8 c.c. $N/100$ $Na_2S_2O_3$ = $C_2H_3O_2Br : 0·98\ Na_2S_2O_3$.

This reaction proceeds much more slowly than those just described. The temperature quotient is smaller.

TABLE IV.—*Sodium Bromoacetate.*

Temperature 25°.

5 c.c. titrated. I = 0·00985 *N*.

Time.	($Na_2S_2O_3$).	($C_2H_2O_2BrNa$).	$K \times C_\infty$.
0	22·8	12·7	—
5	20·95	10·85	0·0063
15	18·4	8·3	0·0061
33	15·6	5·5	0·0060
50	14·0	3·9	0·0060
75	12·5	2·4	0·0062
∞	10·1	0·0	—
		Mean............	0·0061

$K = 0·305$
Another expt. gave $K = 0·315$

Temperature 35°.

10 c.c. titrated. I = 0·00955 *N*.

Time.	($Na_2S_2O_3$).	($C_2H_2O_2BrNa$).	$K \times C_\infty$.
0	31·7	21·1	—
5	27·7	17·1	0·0065
15	22·35	11·75	0·0068
25	19·35	8·75	0·0067
40	16·45	5·85	0·0068
70	13·6	3·0	0·0069
∞	10·6	0·0	—
		Mean............	0·00675

$K = 0·67$

Temperature.	*K*.
25°	0·310
35	0·67
40	0·96
50	1·95

Temperature quotient.

$K_{35}/K_{25} = 2·15$
$(K_{40}/K_{25})^{2/3} = 2·15$
$K_{40}/K_{50} = 2·05$
Mean...... 2·1

The chlorine-substituted acetates react similarly to the bromine and iodine derivatives, but much more slowly. In the case of the reaction with sodium chloroacetate, velocity measurements had to be made at a higher temperature (50—60°).

0·0700 gram $C_4H_7O_2Cl$ required 57·3 c.c. *N*/100 $Na_2S_2O_3$ = $C_4H_7O_2Cl : 1·00\ Na_2S_2O_3$.
0·0688 gram $C_4H_7O_2Cl$ required 54·7 c.c. *N*/100 $Na_2S_2O_3$ = $C_4H_7O_2Cl : 0·98\ Na_2S_2O_3$.
0·0360 gram $C_3H_5O_2Cl$ required 32·2 c.c. *N*/100 $Na_2S_2O_3$ = $C_3H_5O_2Cl : 0·97\ Na_2S_2O_3$.
0·0765 gram $C_3H_5O_2Cl$ required 69·0 c.c. *N*/100 $Na_2S_2O_3$ = $C_3H_5O_2Cl : 0·98\ Na_2S_2O_3$.
0·0748 gram $C_2H_3O_2Cl$ required 73·0 c.c. *N*/100 $Na_2S_2O_3$ = $C_2H_3O_2Cl : 0·92\ Na_2S_2O_3$.

The reaction with sodium chloroacetate is probably accompanied by some side reaction which uses up about 8 per cent. of the chloroacetate, but this small disturbance would only slightly influence the velocity constants.

TABLE V.—*Ethyl Chloroacetate.*

Temperature 25°.

3 c.c. titrated. I = 0·00905 *N*.

Time.	($Na_2S_2O_3$).	($C_4H_7O_2Cl$).	$K \times C_\infty$.
0	24·5	15·0	—
10	23·1	13·6	0·00171
31	20·6	11·1	0·00179
60	18·35	8·85	0·00173
134	14·9	5·4	0·00170
215	12·8	3·3	0·00175
∞	9·5	0·0	—
		Mean............	0·00174

K = 0·061
Other expts. gave K = 0·060, 0·058
Mean......... 0·060

Temperature 35°.

5 c.c. titrated. I = 0·00965 *N*.

Time.	($Na_2S_2O_3$).	($C_4H_7O_2Cl$).	$K \times C_\infty$.
0	23·7	28·1	—
5	21·35	25·75	0·00148
15	17·85	22·25	0·00145
30	14·0	18·4	0·00149
50	10·8	15·2	0·00149
121	5·65	10·05	0·00146
∞	0·0	4·4	—
		Mean............	0·00147

K = 0·173

Temperature quotient = 2·9.

TABLE VI.—*Methyl Chloroacetate.*

Temperature 25°.

3 c.c. titrated. I = 0·00975 *N*.

Time.	($Na_2S_2O_3$).	($C_3H_5O_2Cl$).	$K \times C_\infty$.
0	19·8	16·8	—
10	18·5	15·5	0·00055
25	16·8	13·8	0·00056
40	15·5	12·5	0·00055
70	13·35	10·35	0·00056
100	11·7	8·7	0·00057
310	6·9	3·9	0·00057
	3·0	0·0	—
		Mean......... ..	0·00056

K = 0·057
Another expt. gave K = 0·060
Mean... ..... 0·059

Temperature 35°.

5 c.c. titrated. I = 0·00965 *N*.

Time.	($Na_2S_2O_3$).	($C_3H_5O_2Cl$).	$K \times C_\infty$.
0	21·1	28·5	—
15	15·8	23·2	0·00242
26	13·35	20·75	0·00235
40	11·0	18·4	0·00232
61	8·5	15·9	0·00232
100	5·7	13·1	0·00231
∞	0·0	7·4	—
		Mean...........	0·00234

K = 0·165
Other expts. gave K = 0·160, 0·165
Mean .... 0·165

Temperature quotient = 2·8.

TABLE VII.—*Sodium Chloroacetate.*

Temperature 50°.

2·98 c.c. titrated. I = 0·0094 *N.*

Time.	($Na_2S_2O_3$).	($C_2H_2O_2ClNa$).	$K \times C_\infty$.
0	30·6	24·2	—
20	26·85	20·45	0·00081
50	23·2	16·8	0·00077
100	18·6	12·2	0·00081
170	15·0	8·6	0·00082
280	11·95	5·55	0·00083
510	9·0	2·6	0·00086
∞	6·4	0·0	—
		Mean............	0·00082

K = 0·0405

Other expts. gave
K = 0·039, 0·0395, 0·0395

Mean......... 0·0395

Temperature 60°.

2·98 c.c. titrated. I = 0·0094 *N.*

Time.	($Na_2S_2O_3$).	($C_2H_2O_2ClNa$).	$K \times C_\infty$.
0	33·5	8·5	—
10	31·8	6·8	0·0074
25	29·8	4·8	0·0079
45	28·55	3·55	0·0069
95	26·3	1·3	0·0074
∞	25·0	0·0	—
		Mean............	0·0074

K = 0·094

Another expt. gave *K* = 0·100

Mean......... 0·097

Temperature quotient = 2·45.

$$\text{Calculated velocity at } 25° = \frac{0·0395}{(2·45)^{5/2}} = 0·0042$$

The following table is a summary of the velocity constants of the seven reactions just described :

TABLE VIII.—*Velocity Constants at* 25°.

	Iodoacetate.	Bromoacetate.	Chloroacetate.
Ethyl	7·0 (2·75)	6·4 (2·75)	0·060 (2·9)
Methyl	—	5·85 (2·8)	0·059 (2·8)
Sodium	—	0·315 (2·1)	0·0042 (2·45)
Methyl iodide	0·90 (3·0)		

The iodo- and bromo-esters are several times more reactive than methyl iodide, and the reactivity of the iodine, bromine, and chlorine derivatives is roughly in the ratio 1 : 1 : 1/100, compared to 1 : 1 : 1/40 in the case of the methyl haloids. It is noteworthy that the bromoacetic and chloroacetic ions are considerably less active than the corresponding undissociated esters. The temperature quotients (given in brackets) for the reactions with the five esters are within experimental limits equal to 2·8. In the case of the sodium salts, this value is appreciably smaller.

The great reactivity of these substituted acetic esters renders it possible to carry out velocity measurements in very dilute solutions, thus adding considerably to the ease of the investigation. It was therefore found convenient at this point to investigate the action of other metallic thiosulphates, and decide whether these reactions are

primarily connected with the S_2O_3'' ion, or whether the NaS_2O_3' ion or undissociated $Na_2S_2O_3$ also takes part in the reaction.

Ethyl bromoacetate was the haloid selected for this purpose. Experiments were first carried out with metallic thiosulphates, which show no tendency to form complex salts, and which probably are for the main part dissociated in dilute solution.

The following table shows that the velocity constants obtained by the use of such salts approximate to that found for sodium thiosulphate.

TABLE IX.—Temperature 25°.

Potassium Thiosulphate.

50 c.c. titrated. I = 0·00945 *N.*

Time.	($K_2S_2O_3$).	($C_4H_7O_2Br$).	$K \times C_\infty$.
0	21·65	15·75	—
5	17·9	12·0	0·0071
10	15·5	9·6	0·0070
20	12·5	6·6	0·0070
30	10·7	4·8	0·0070
45	9·1	3·2	0·0070
∞	5·9	0·0	—
		Mean............	0·0070

$K = 6·3$
Another expt. gave $K = 6·3$

Ammonium Thiosulphate.

50 c.c. titrated. I = 0·00945 *N.*

Time.	[$(NH_4)_2S_2O_3$].	($C_4H_7O_2Br$).	$K \times C_\infty$.
0	26·4	14·8	—
5	22·2	10·6	0·0140
15	17·9	6·3	0·0135
25	15·65	4·05	0·0134
40	14·05	2·45	0·0127
55	13·0	1·4	0·0130
∞	11·6	0·0	—
		Mean	0·0133

$K = 6·1$

Barium Thiosulphate.

50 c.c. titrated. I = 0·0109 *N.*

Time.	(BaS_2O_3).	($C_4H_7O_2Br$).	$K \times C_\infty$.
0	23·0	21·3	—
5	17·7	16·0	0·00212
10·5	14·0	12·3	0·00218
15	12·0	10·3	0·00221
25	9·2	7·5	0·00222
35	7·55	5·85	0·00221
∞	1·7	0·0	—
		Mean............	0·00219

$K = 5·9$
Another expt. gave $K = 5·5$

Strontium Thiosulphate.

50 c.c. titrated. I = 0·00945 *N.*

Time.	(SrS_2O_3).	($C_4H_7O_2Br$).	$K \times C_\infty$.
0	16·6	14·6	—
5	13·95	11·95	0·00220
10	12·1	10·1	0·00228
20	9·7	7·7	0·00223
30	8·1	6·1	0·00225
50	6·4	4·4	0·00214
∞	2·0	0·0	—
		Mean............	0·00222

$K = 5·9$
Another expt. gave $K = 5·5$

Experiments were then carried out with some complex thiosulphates. The effect of the addition of silver nitrate on the velocity of reaction between sodium thiosulphate and ethyl bromoacetate was first investigated. The presence of silver nitrate has no influence on the end-point of the titration of sodium thiosulphate by an iodine solution, and the reaction could, therefore, be followed by this titration.

The results obtained by such measurements are given in the following tables.

Table X shows that the addition of small quantities of silver nitrate decreases the activity of the thiosulphate in such a way as to render inactive a portion of the thiosulphate, corresponding with the formation of the compound $Na_3Ag(S_2O_3)_2$. The values of K are calculated not from the iodine titre, but from the titre of the uncombined sodium thiosulphate, that is, the difference between the iodine titre and that corresponding to the concentration of the salt $Na_3Ag(S_2O_3)_2$.

The values of K so obtained approximate to 6·4, the value found for pure sodium thiosulphate.

The concentration of the ester in these experiments is found by a further addition of sodium thiosulphate, or by adding potassium iodide and decomposing the complex salt with precipitation of silver iodide.

TABLE X.—*The Effect of the Addition of Small Quantities of Silver Nitrate.*

50 c.c. titrated. I = 0·0111*N*. Temperature = 25°.

$AgNO_3$.	Time.	I. titre.	$(Na_2S_2O_3)$.	(Ester).	$K \times C_\infty$.
0·00100	0	31·8	22·8	25·1	—
	5	25·4	16·4	18·7	0·0032
	10	21·6	12·6	14·9	0·0031
	15	19·35	10·35	12·65	0·0030
	25	16·4	7·4	9·7	0·0030
	35	14·7	5·7	8·0	0·0030
$Na_3Ag(S_2O_3)_2$	=	9·0	0·0	2·3	—
	∞	6·7		0·0	
				Mean...........	0·0031, K=6·1
0·00100	0	24·3	15·3	18·0	—
	5	20·8	11·8	14·5	0·0038
	10	18·5	9·5	12·2	0·0038
	20	15·9	6·9	9·6	0·0036
	30	14·3	5·3	8·0	0·0036
$Na_3Ag(S_2O_3)_2$	=	9·0	0·0	2·7	—
	∞	6·3		0·0	
				Mean...........	0·0037, K=6·2
0·00250	0	37·2	14·7	24·7	—
	5	32·8	10·3	20·3	0·0139
	10	30·15	7·65	17·65	0·0138
	20	27·0	4·5	14·5	0·0141
$Na_3Ag(S_2O_3)_2$	=	22·5	0·0	10·0	—
	∞	12·5		0·0	
				Mean...........	0·00139, K=6·3

This result shows that the reactivity of trisodium silver thiosulphate is small compared with that of sodium thiosulphate and negligible in the presence of moderate excess of the latter salt.

Sodium thiosulphate and silver nitrate were then mixed in such proportions that excess of silver nitrate was present after the forma-

tion of the complex salt $Na_3Ag(S_2O_3)_2$. The initial velocity of the reaction of this mixture on ethyl bromoacetate was measured and shown to be comparatively small.

TABLE XI.—*The Effect of the Addition of a Large Quantity of Silver Nitrate.*

Temperature = 25°, $AgNO_3$ = 0·0040 gram ($AgNO_3$) per litre. 25 c.c. titrated. I = 0·0110 *N*.

Time.	I. titre.	(Ester).	$K \times C_\infty$.
0	15·35	14·4	—
10	14·55	13·6	[0·00017]
20	13·95	13·0	[0·00015]
40	12·95	12·0	0·000135 K=0·32
∞	0·95	0·0	—

Mean, I titre = 14·15 c.c. = 0·0062 gram ($Na_2S_2O_3$) per litre.

Percentage of thiosulphate present as $S_2O_3'' = \frac{0·32 \times 100}{6·4} = 5·0$ per cent.

This table shows that a mixture of the two salts in the proportion 0·0040 $AgNO_3$: 0·0062 $Na_2S_2O_3$ has only one-twentieth the activity of sodium thiosulphate. It is probable that the complex salt is partially dissociated according to the equation $Na_3Ag(S_2O_3)_2 \rightleftarrows Na_2S_2O_3 + NaAgS_2O_3$, and that the reaction depends on the presence of a small quantity of uncombined sodium thiosulphate. As the salts are in dilute aqueous solution, the equilibrium is better indicated by $Ag(S_2O_3)_2''' \rightleftarrows AgS_2O_3' + S_2O_3''$, the uncombined thiosulphate being represented by the S_2O_3'' ion. The fact that the addition of silver nitrate lowers the activity so considerably is strong evidence in support of the view that the reaction is primarily connected with the S_2O_3'' ion.

The ions $Ag(S_2O_3)_2'''$, AgS_2O_3' and the corresponding undissociated salts either do not react, or react with a relatively much smaller velocity. This view is also supported by experiments made with the complex lead thiosulphates where similar results are obtained.

A consideration of these results with those obtained with sodium, potassium, ammonium, barium, and strontium thiosulphates (Table IX) renders probable the assumption that the velocity of these reactions is strictly proportional to the concentration of the S_2O_3'' ion. If this proportionality holds, we have a dynamic method of measuring concentrations of S_2O_3'' ions similar to that by which concentrations of OH′ ion can be measured by the velocity of saponification of ethyl acetate. This method may prove of value in a study of the stability of the complex thiosulphates, and gives a means of amplifying the results obtained by solubility and electromotive force measurements (G. Bodländer, *Ber.*, 1903, **36**, 3933; H. Euler, *Ber.*, 1904, **37**, 1704).

Solutions of sodium thiosulphate with excess of silver nitrate soon turn brown, and are therefore not convenient for investigation, but lead thiosulphate solutions are quite stable at 25°, and it was hoped by an investigation of the activity of sodium thiosulphate in the presence of varying quantities of lead nitrate to calculate the dissociation constants of lead and sodium lead thiosulphates,

$$PbS_2O_3 \rightleftarrows Pb^{\cdot\cdot} + S_2O_3'',\ Pb(S_2O_3)_2'' \rightleftarrows PbS_2O_3 + S_2O_3''.$$

By adding a large excess of lead nitrate to sodium thiosulphate, and by measuring the concentration of the S_2O_3'' ion by velocity experiments, the value of the first equilibrium constant was found to be $K_1 = [Pb^{\cdot\cdot}][S_2O_3'']/[PbS_2O_3] = 1{\cdot}5 \times 10^{-4}$ (Table XII). By adding a relatively small quantity of lead nitrate, the complex salt $Na_2Pb(S_2O_3)_2$ is formed quantitatively (Table XIII). With concentrations of lead nitrate intermediate between those employed in these two experiments, both dissociations come into consideration. If K_1 is assumed to have the value $1{\cdot}5 \times 10^{-4}$, the value of the second equilibrium constant, $[PbS_2O_3][S_2O_3'']/[Pb(S_2O_3)_2'']$, was found to be of the order 10^{-3}. Details of these measurements are not given, as the method affords only approximate values of the constant.

The method of investigation was the same as that employed in finding the effect of the addition of silver nitrate (Tables X, XI). Thiosulphates can be estimated in the presence of lead salts by titration with iodine solution, and the concentration of the ester can be found by decomposing the complex salt with potassium iodide and by further addition of sodium thiosulphate.

In making up the solutions, different amounts of a lead nitrate solution containing $Pb(NO_3)_2/20$ grams per litre were used. In the experiment given in Table XII, 50 c.c. of lead nitrate solution, sufficient sodium thiosulphate to give an approximately $N/1000$ solution, and a little more than the equivalent of ethyl bromoacetate were mixed and made up to one litre, and the initial rate of the reaction measured at 25°.

The concentration of the S_2O_3'' was calculated from the value of the velocity constant K by comparing it to 6·4, the value found for sodium thiosulphate.

If a, b, and c are respectively the concentrations of PbS_2O_3, S_2O_3'' and $Pb^{\cdot\cdot}$, then

$a + b$ = concentration of thiosulphate found by titration,

$a + c$ = " " lead nitrate,

$b = \dfrac{K(a+b)}{6{\cdot}4}$, where K is the velocity constant.

From these three equations, a, b, and c can be calculated and the

value of the equilibrium constant ($K_1 = bc/a$) found. A summary of four such experiments is also given in the following table:

TABLE XII.—*The Equilibrium* $PbS_2O_3 \rightleftarrows Pb^{\cdot\cdot} + S_2O_3''$.

50 c.c. $Pb(NO_3)_2$ solution in 1 litre, $a + c = 0·00250$. 100 c.c. titrated. I = 0·0094 *N*. Temperature 25°.

Time.	I. titre.	(Ester).	$K \times C_\infty$.
0	13·95	18·1	—
210	9·75	13·9	0·00195
∞	0·0	4·15	—

$$K = \frac{0·00195 \times 100}{4·15 \times 0·0094} = 0·50.$$

Mean, I. titre = 11·85.

$$\therefore a + b = \frac{11·85 \times 0·0094}{100} = 0·001115. \qquad b = \frac{0·50\ (a+b)}{6·4} = 0·000087.$$

$$a + c = 0·00250. \qquad \therefore a = 0·00103,\ c = 0·00147.$$

$$K_1 = bc/a = 1·24 \times 10^{-4}.$$

Summary.

$a+c$.	$a+b$.	b.	a.	c.	$K_1 = bc/a$.
0·00250	0·001115	0·000087	0·00103	0·00147	$1·24 \times 10^{-4}$
0·00250	0·001161	0·000090	0·00107	0·00143	$1·20 \times 10^{-4}$
0·00300	0·00100	0·000060	0·00094	0·00206	$1·32 \times 10^{-4}$
0·00300	0·001025	0·000064	0·00096	0·00204	$1·36 \times 10^{-4}$

Corrected value of $K_1 = 1·5 \times 10^{-4}$.

In the calculation of K_1 no account is taken of the formation of the $Pb(S_2O_3)_2''$ ion, which is present in small concentration in the solutions. From other experiments, the value of the equilibrium constant, $[PbS_2O_3][S_2O_3'']/[Pb(S_2O_3)_2'']$, was found to be of the order 10^{-3}. In the four experiments summarised in Table XII, the value $a = [PbS_2O_3]$ is about 10^{-3}, and therefore the concentration of the $Pb(S_2O_3)_2''$ ion is approximately equal to that of the S_2O_3'' ion. Applying the small correction, the mean value of K_1 was found to be $1·5 \times 10^{-4}$.

When small quantities of lead nitrate are added to a sodium thiosulphate solution, part of the thiosulphate is rendered inactive, this amount corresponding with the formation of the complex disodium lead thiosulphate, $Na_2Pb(S_2O_3)_2$. If the titre of this salt is subtracted from the iodine titre to obtain the concentration of free sodium thiosulphate, and the calculation of the velocity constant made as in table X, the value of K approaches to that found for pure sodium thiosulphate (6·4). The sodium lead thiosulphate is, however, appreciably dissociated into lead and sodium thiosulphates, for even with moderate excess of sodium thiosulphate higher values of K are obtained.

TABLE XIII.

50 c.c. titrated. I = 0·01065 *N*. Temperature = 25°.

$Pb(NO_3)_2$.	Time.	titre.	$(Na_2S_2O_3)$.	(Ester).	$K \times C_\infty$.
0·0010	0	28·05	18·65	15·05	—
	5	24·4	15·0	11·4	0·0052
	10	22·0	12·6	9·0	0·0053
	20	19·1	9·7	6·1	0·0054
	30	17·5	8·1	4·5	0·0054
	∞	13·0	3·6	0·0	—
$Na_2Pb(S_2O_3)_2$	=	9·4	0·0		
				Mean......... ..	0·0053
			$K = 6·9$		

The velocity of the reaction between lead thiosulphate and ethyl bromoacetate has also been measured. This salt is soluble to about 1/1000 *N*, and the solution contains probably appreciable quantities of $Pb^{\cdot\cdot}$, PoS_2O_3, $Pb(S_2O_3)_2''$, and S_2O_3''.

TABLE XIV.—*Lead Thiosulphate.*

Temperature 25°.

100 c.c. titrated. I = 0·01065 *N*.

Time.	(PbS_2O_3).	(Ester).	$K \times C_\infty$.	Time.	(PbS_2O_3).	(Ester).	$K \times C_\infty$.
0	11·95	17·75	—	0	9·95	16·75	—
60	9·95	15·75	0·00046	60	8·35	15·15	0·00054
∞	0·0	5·8	—	∞	0·0	6·8	—
			$K = 0·75$				$K = 0·75$

Besides lead thiosulphate, salts of the anion, $Pb(S_2O_3)''$, undoubtedly exist, tetrasodium lead thiosulphate, $Na_4Pb(S_2O_3)_3$, has been isolated, and indications of higher complex salts have been obtained.

According to measurements described in this paper, the values of the equilibrium constants are found to be

$$[Pb^{\cdot\cdot}][S_2O_3'']/[PbS_2O_3] = 1·5 \times 10^{-4},$$
$$[PbS_2O_3][S_2O_3'']/[Pb(S_2O_3)_2''] = 10^{-3} \text{ (approximately).}$$

More complex salts could not be detected, and probably do not exist in dilute solution. H. Euler (*loc. cit.*), by estimating the concentration of $Pb^{\cdot\cdot}$ ion in presence of large quantities of sodium thiosulphate, gives the value of the constant,

$$[Pb^{\cdot\cdot}][S_2O_3'']^2[NaS_2O_3']^2/[PbNa_2(S_2O_3)_4''''] = 5 \times 10^{-8}.$$

This value is not far removed from the product of the above constants, and is therefore in agreement with the supposition that the higher complex salts easily dissociate into the more stable lead and disodium lead thiosulphates.

The velocity constants of the reaction between ethyl bromoacetate and different thiosulphates may with advantage be summarised, for it is from these numbers the conclusion is drawn that the reaction velocities are proportional to the concentration of the S_2O_3'' ion. In the following table K is independent of concentration in the first five cases; in the last three, concentrations are given in grams × formula weight / per litre.

TABLE XV.—*Velocity Constants at* 25°.

Thiosulphate.	K.		Thiosulphate.	K.
$Na_2S_2O_3$	6·4		SrS_2O_3	5·7
$K_2S_2O_3$	6·3	0·0062	$Na_2S_2O_3 + 0·0040\ AgNO_3$	0·32
$(NH_4)_2S_2O_3$	6·1	0·001115	$Na_2S_2O_3 + 0·0025\ Pb(NO_3)_2$ ...	0·50
BaS_2O_3	5·7	0·001	PbS_2O_3	0·75

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LX.—*The Kinetics of Chemical Changes which are Reversible. The Decomposition of* as-*Dimethylcarbamide.*

By CHARLES EDWARD FAWSITT.

WHEN a chemical reaction is not completely unidirectional but reaches a state of equilibrium at some intermediate point, then, writing the equation of the reaction:

$$m_1A_1 + m_2A_2 + m_3A_3 \ldots \rightleftarrows n_1B_1 + n_2B_2 \ldots \quad (1),$$

the velocity of reaction is represented by

$$-\frac{da_1}{dt} = ka_1^{m_1}a_2^{m_2}a_3^{m} \ldots - k'b_1^{n_1}b_2^{n} \ldots \quad (2),$$

where $A_1, A_2 \ldots B_1, B_2 \ldots$ are the substances involved,
$a_1 a_2 \ldots b_1 b_2 \ldots$ the concentrations of these substances,
"t" the time, $m_1, m_2 \ldots n_1, n_2 \ldots$ the number of molecules of

the different substances, and $k_1 k'$ the velocity constants of the two opposing reactions.

In some simple examples, it is possible to integrate equation (2) and to apply the formulæ to experimental cases. The integration gives an equation containing both k and k', and this can only be solved for one or other if the equilibrium constant k/k' is known. The equilibrium constant is obtained by a determination of the relative amounts of substance present after the attainment of equilibrium. As, however, this attainment of equilibrium is a somewhat slow process, and as there may be some side-reaction or secondary change accompanying the main reaction, the determination of the equilibrium constant is sometimes a difficult matter.

Another method of attacking such problems of chemical kinetics is to arrange so that the inverse reaction shall not be allowed to take effect. If one can arrange to destroy or remove from the sphere of action the reaction products as soon as they are formed, then the effect of the inverse reaction is completely eliminated.

Reactions to which this method can be applied are somewhat limited in number, but the author has already shown that the decompositions of carbamide (*Zeit. physikal. Chem.*, 1902, **41**, 601) and methylcarbamide (Trans., 1904, **86**, 1581) with acids are reactions which approximate to the case where the right-hand term of equation (2) may be neglected in the integration, and it was expected that *as*-dimethylcarbamide would probably behave in a similar fashion. The decomposition of this class of amides in aqueous solution may be represented by

$$\frac{dx}{dt} = k(A - x) - k'x^2 \quad \ldots\ldots\ldots\ldots\ldots\ldots \quad (3),$$

the decomposition product being a cyanate, and x, $A - x$, being the concentration of decomposed and undecomposed substance at time "t."

Whilst acids appear to have no direct action on these amides, the cyanate which is formed from the amide decomposes very quickly under the action of acid, and the equation (3) approximates to the case

$$\frac{dx}{dt} = k(A - x).$$

The integral of this is:

$$k = \frac{1}{t}\log_\epsilon\frac{A}{A - x}.$$

Constants were calculated in the case of carbamide and methylcarbamide, and also in the present instance of *as*-dimethylcarbamide according to the above formula, and the constant value of the numbers obtained was unquestionable.

The value of "k" has already been calculated from the data obtained by a determination of k' and $\bar{K}$ the equilibrium constant (Walker and Hambly, Trans., 1895, **67**, 746; Walker and Appleyard, Trans., 1896, **69**, 193). Whilst the value of k deduced by the latter method and the number obtained experimentally by the author agree well in the case of carbamide, the agreement is not quite so good in the cases of methylcarbamide and *as*-dimethylcarbamide, although the numbers obtained are of the same order.

Experimental.

The method of experiment adopted was the same as that used for methylcarbamide, and the temperature at which the decompositions were carried out was 97·8° unless otherwise stated.

The *as*-dimethylcarbamide was obtained from Kahlbaum, and, as it seemed very pure (m. p. 182°), it was used for the decomposition experiments without recrystallisation. The results of the experiments were calculated on the assumption that the reaction was one of the first order.

The Reaction between Dimethylcarbamide and Acids.—As in the previous work hydrochloric acid was found to be as suitable as any other acid, it was used in this case exclusively. The reaction with hydrochloric acid might be expected to go according to the following equation:

$$CO(NH_2)\cdot N(CH_3)_2 + 2HCl + H_2O = CO_2 + NH_4Cl + NH_2(CH_3)_2Cl.$$

To test this, a few grams of *as*-dimethylcarbamide were heated with hydrochloric acid solution for 3 days at 97·8° in a tube covered with melted paraffin to prevent evaporation. The paraffin was afterwards removed and the solution evaporated to dryness on the water-bath, and further dried in a vacuum desiccator. The resulting mass was then treated with warm chloroform and filtered. The residue was recrystallised from a mixture of water and alcohol.

0·1484 of this product required 0·470 $AgNO_3$ (Volhard's method).
0·1484 NH_4Cl should require 0·471 $AgNO_3$.

The filtrate (after extracting with chloroform) was evaporated to dryness on the water-bath and dried in a vacuum desiccator over sulphuric acid until the weight was constant.

0·341 required 0·706 $AgNO_3$.
0·341 $NH_2(CH_3)_2Cl$ should require 0·7105 $AgNO_3$.

The additional fact that the *as*-dimethylcarbamide, when heated for

a sufficiently long time, neutralises hydrochloric acid in the ratio of $CO(NH_2)\cdot N(CH_3)_2$ to $2HCl$, leads to the belief that the reaction does proceed according to the above equation.

The velocity determinations are given below, the time is expressed in minutes, A is the initial concentration of *as*-dimethylcarbamide, x is the concentration of decomposed substance, and k is $= \frac{1}{t} \log_{10} \frac{A}{A-x}$; $A - x_{(1)}$ and $A - x_{(2)}$ are two experiments, $A - x_{(m)}$ being the mean.

Table I.

$N/16$-*Dimethylcarbamide* + $N/16$-HCl.

Time.	$A - x$.	$k \times 10^4$.
0	10·69	—
16·5	8·70	54
23·5	7·94	55
32·5	7·21	53
59	5·22	53
84	3·79	54

Table II.

$N/16$-*Dimethylcarbamide* + $N/8$-HCl.

Time.	$A - x$.	$k \times 10^4$.
0	10·62	—
31·5	7·33	51
47·5	6·12	50
120	2·51	52
167	1·37	53

Table III.

$N/16$-*Dimethylcarbamide* + $N/4$-HCl.

Time.	$A - x_{(1)}$.	$A - x_{(2)}$.	$A - x_{(m)}$.	$k \times 10^4$.
0	10·69	10·69	10·69	—
20·5	8·57	8·70	8·64	45
38·5	7·12	7·18	7·15	45
59	5·77	5·79	5·78	45
110	3·41	3·51	3·46	45

Table IV.

$N/16$-*Dimethylcarbamide* + $N/2$-HCl.

Time.	$A - x$.	$k \times 10^4$.
0	10·69	—
31·5	8·20	36
47	7·27	36
96	4·86	36
161	2·85	36

Whilst the constants in the different tables show that the reaction is undoubtedly one of the first order, it will be noticed that the velocity constant decreases with increasing concentration of acid. In this respect, the behaviour of dimethylcarbamide is identical with that of carbamide and methylcarbamide. The increasing concentration of acid depresses the concentration of free dimethylcarbamide, and thus apparently diminishes the reaction velocity coefficient.

A determination of the velocity constant at 59·6° was made so as to compare the value obtained with that found by Walker and Appleyard (Trans., 1896, 69, 193).

TABLE V.

N/16-*Dimethylcarbamide* + *N*/16-HCl.

Time.	$A-x$.	$k \times 10^6$.
0	9·53	—
1576	8·10	44
4061	6·63	39
5763	5·56	41
7120	4·86	41
9900	3·83	40

Taking the average value as 41, the real * value of k is equal to $\frac{41 \times 10^{-6}}{0·4343} = 0·000094$.

This is considerably less than the value obtained by Walker and Appleyard, which was 0·00073, so that there is no doubt that the velocity with which the cyanate is destroyed by the acid in the above experiments is quite comparable with the velocity at which the cyanate is formed from the dimethylcarbamide, and is not instantaneous, as would be necessary if the time value of the constant were to be obtained. The results of the decomposition with acids show in every respect a strong similarity to those obtained for carbamide and methylcarbamide, and there can be no doubt that all the alkyl derivatives of carbamide decompose in a similar manner to those examples already studied, and that the general equation representing the decomposition of the carbamides by water is $dx/dt = k(A-x) - k'x^2$.

The Decomposition of as-*Dimethylcarbamide by Alkalis.*

The decomposition of cyanates by alkali is a much slower process than the decomposition by acid, and a solution of dimethylcarbamide

* No correction is made for salt formation ; by this correction, k would be raised probably by about 10 per cent.

which has been heated for some time with sodium or potassium hydroxide shows the presence of a large quantity of undecomposed cyanate. The reaction might therefore be supposed to take place with a considerably smaller velocity than when acids are used, but just as in the case of the other carbamides we must assume that, in addition to the decomposition of the amide by way of cyanate, there is also a direct action of the alkali on the amide (saponification). This direct saponification increases with the concentration of alkali employed.

The following results were obtained by heating the solutions in platinum tubes enclosed in glass tubing. With such experiments, it is more difficult to get two parallel experiments to agree than in the previous experiments.

This is due to the fact that the velocity depends somewhat on the "gas" space, that is, the space not occupied by the liquid. It is somewhat difficult to render this space constant when one tube is thus enclosed in another.

Table VI.

N/2-Dimethylcarbamide + N/2-Potassium Hydroxide.

Time.	$A - x_{(1)}$.	$A - x_{(2)}$.	$A - x_{(m)}$.	$K \times 10^4$.
0	10·00	10·00	10·00	—
35	7·48	—	7·48	36
85	5·66	—	5·66	29
225	2·70	3·54	3·12	22

Table VII.

N/2-Dimethylcarbamide + 3N/2-Potassium Hydroxide.

Time.	$A - x_{(1)}$.	$A - x_{(2)}$.	$A - x_{(m)}$.	$K \times 10^4$.
0	10·00	10·00	10·00	—
45	5·65	5·42	5·52	57
203	1·84	1·70	1·77	37

Table VIII.

N/2-Dimethylcarbamide + 3N/2-Sodium Hydroxide.

Time.	$A - x_{(1)}$.	$A - x_{(2)}$.	$A - x_{(m)}$.	$K \times 10^4$.
0	10·00	10·00	10·00	—
55	5·96	5·80	5·88	42
167	2·02	—	2·02	42
218	1·50	—	1·50	38
1408	0·22	—	0·22	—

The velocity increases a little with increased concentration of alkali, but the increase of velocity is by no means proportional to the increase of concentration, and it must be concluded, as in the case of the carbamides hitherto studied, that even concentrated alkali effects a direct hydrolysis only with great difficulty.

Summary of Results.

The decomposition of the substances of the carbamide group by acids is due to a transformation into cyanate, which is then decomposed by the acid. The transformation into cyanate is proportional to the concentration of the amide.

Whilst a small increase of the acid concentration, starting from a dilute solution, does not affect the velocity of decomposition of these amides, the effect of a large increase of concentration is to retard the velocity. This retardation is due to the removal of some amide from the active amount of decomposing substance owing to salt formation.

as-Dimethylcarbamide decomposes with acids at about six to seven times the rate at which carbamide decomposes. The velocity of decomposition of *as*-dimethylcarbamide with alkalis is of the same order as that with acids.

I desire to express my thanks to the Executive Committee of the Carnegie Trust for the Universities of Scotland for a grant to defray the expenses of this research.

UNIVERSITY OF GLASGOW.



Johannes Wislicenus

WISLICENUS MEMORIAL LECTURE.[1]

By W. H. PERKIN, jun.

WHEN Johannes Wislicenus passed away, two years ago, an acute sense of loss was felt, not only in the world of Science, where his name had long been placed among those of the great organic chemists, but also in other fields where men of science have but seldom left deep impressions of their personal influence.

Innate qualities, obscured as they so often may be by others adventitious or assumed, are not always easy to trace unless history gives the clues. But the character of Wislicenus was even higher than his scientific work, and I am tempted to dwell upon it, rather than on the achievements which are familiar to chemists, because the simplicity and personal force of the man were known to comparatively few, while his chemical fame was, of course, world-wide.

During the seventeenth century, a family of Poles, victims of the intolerant spirit and religious persecution of the time, wandered homeless into Germany, and finding at last congenial surroundings in Schönburg, where for many generations afterwards the family made their home, they took up priestly duties and devoted their lives to the welfare of their fellow-men. Among their descendants was Gustav Adolf Wislicenus, a man who sustained the family traditions and shone with all the fine qualities of his race. The story of his life reveals the fearlessness of his character, and aids us in forming a true conception of the forces in the composition of his son Johannes, for between the two men there was more in common than is usual between father and son.

Gustav Adolf Wislicenus felt the weight of religious oppression at an early age, for whilst yet a student he was condemned to imprisonment on account of his connection with certain sectarian societies. This was in 1824, and it was not until 1829, five years later, that his friends were able to obtain for him a formal pardon and the remission of the remainder of his sentence. After his release he chose the vocation of a Lutheran priest, and from 1834 pursued this calling at the little village of Klein-Eichstädt, near Querfurt, until he was preferred to the Neumarkt-Kirche at Halle in the year 1841.

This period in Prussia was marked by the rapid growth of popular antagonism to the efforts made by the more powerful of the clergy to regulate the form of religious worship throughout the country, and

[1] The author wishes to acknowledge the very valuable assistance which he received from Dr. A. Lapworth while compiling this Memorial Lecture.

this feeling first reached its climax in Saxony, and in particular among the rationalistic clergy. With these pastor Wislicenus threw in his lot. At the great meeting of "Lichtfreunde" at Cöthen in 1844, he gave full expression to his revolutionary views on the foundations of faith, the result being that the supporters of the new ideas found themselves denounced as traitors and their meetings proscribed, Wislicenus himself being expelled from his office two years later.

The growth of the spirit of independence had led to the formation in different parts of the country of a number of 'free congregations,' and the foundation of one of these at Halle was the first object which Wislicenus set himself to attain after his loss of position. Political movement culminated in the revolution of 1848 and the Frankfort Parliament. In the latter, which was a Parliament without statesmen, we find Gustav Wislicenus and many other leaders in the free religious movement occupying positions of prominence and playing active parts.

At this time Johannes Wislicenus was about fifteen years of age. He was born at Klein-Eichstädt on June 24, 1835, the year following his father's appointment at that place, and, when Halle became the home of the family, was sent to the Realschule der Frankeschen Stiftungen, where his marked zeal was followed by well deserved success. He was one of a numerous family whom the expulsion of the father from office threw into dire distress, and the boy's experience of some of the bitter hardships of life helped to steel his youthful frame. Even in these early days he took first place among his comrades and excelled in swimming and gymnastics, but above all in his favourite study, the German language.

Science early attracted his special regard, and on passing from school to the university he soon found himself able to pay her the single-hearted devotion she claims. With his appointment as assistant to Professor Heintz in 1853, he finally dedicated himself to chemistry.

His absorbing chemical studies, so auspiciously begun, were not long to be continued without interruption. The family prospects were clouding over, and in this same year the father was condemned to two years' imprisonment as a consequence of the publication of his work "Die Bibel im Lichte der Bildung unserer Zeit." This new disaster left flight the only chance, and, with the help of trusty friends, Gustav succeeded in making his escape, while the family, under the charge of the young Johannes, followed him.

Proceeding first to England, they embarked for the United States. Ill fortune again overtook them, for the vessel in which they set sail was soon discovered to be cholera-stricken. The ship's doctor found his time and energies fully occupied in attending to the first-class

passengers, and, in characteristic manner, it was young Wislicenus who, in this emergency, acted as physician and nurse to the forsaken occupants of the steerage. When all hope of stamping out the scourge at last disappeared, the ship put back to England, where the family lived in straitened circumstances until they were again able to set out for the New World.

The sojourn in America was not of long duration, for at the end of two years they found it possible to return to Europe. During this time the scientific knowledge of Johannes was the means of support on which the family relied, and he was fortunate enough to obtain an appointment as an assistant to Professor Horsford, of Harvard, and afterwards he conducted an analytical laboratory of his own in New York.

Zürich became the headquarters of the family on their return to Europe. The son was able to resume his interrupted scientific career at Halle, under Heintz, whom he rejoined in 1857, and with whom he remained until the autumn of 1859.

The friendship which sprung up between the two chemists lasted until the death of Heintz, twenty years later. Their association was marked by the publication of several joint researches. One of these dealt with a base they isolated from the products obtained by heating aldehyde-ammonia on the water-bath, to which, in the symbols then in use, they assigned the formula $C_{16}H_{13}NO_2$.[1] The compound is that now known as "oxytetraldin," $C_8H_{13}NO$.

A second communication dealt with experiments on goose-gall and the nature of some of its complicated acidic constituents.[2] A third one, of more general interest, resulted in the disappearance from literature of the "aldehydic acid" which Liebig considered was an intermediate step in the oxidation of acetaldehyde to acetic acid. The paper by Heintz and Wislicenus[3] exposed the slender character of Liebig's evidence, and indicated that acetic acid is the only definite product obtained when acetaldehyde is treated with silver oxide in accordance with Liebig's directions.

It was at this time also that the first papers by Wislicenus himself appeared.[4] These dealt with his own views as to the relationship of glycol and glycerine in the light of the type theory which was then the guiding principle of classification.

In 1859 Wislicenus left Halle for Zürich. This step was his reply to the action of the governing body of the Halle Hochschule, who, before allowing him the title of 'Privatdocent,' required him to offer

[1] *Poggendorff's Annalen*, 1858, **105**, 577. [2] *Ibid.*, 1859, **108**, 547.

[3] *Ibid.*, 101.

[4] Halle, *Zeit. Gesammt. Naturw.*, 1859, **13**, 270, 442; **14**, 97; *J. pr. Chem.*, 1859, **77**, 149.

guarantees that he would in future refrain from all public expression of his political opinions. Such an attempt to bring pressure on him was foredoomed to failure. His principles, absorbed first from his father and afterwards from his friends in freedom-loving America, were already firmly fixed; he had come to regard the enunciation of his political and religious principles as part of his life's work, and throughout his career he was ever active in their furtherance.

At Zürich his progress was rapid. He was appointed Professor of Chemistry and Mineralogy, under the Council of the Canton, at the School of Industries, in 1861. Three years later he was made Extraordinary Professor and Director of the Laboratories in the University, and in 1867 Ordinary Professor. In 1870 the Education Council conferred on him the Chair of Chemistry in the Polytechnic, and a year later he was made Director.

In Zürich the problems connected with his investigation of the lactic acids absorbed his special interest. The question of the most suitable formula for the acid, which Scheele had discovered in the eighteenth century, was engaging much attention among chemists and provoking interesting controversy. On some points a preliminary agreement seems to have been attained, but it was generally recognised that searching experimental study was necessary if a final verdict was to be pronounced. The natural development of his earlier research work led Wislicenus to examine the points at issue, and he soon perceived that, to a certain extent, the facts as then known were in harmony with prevailing theories of structure, but that much was left without explanation, and appeared to call for some modification or extension of the existing views.

According to the conceptions of structure in use at that time, two, and only two, isomeric lactic acids should be capable of existence, and these should be characterised by complete disparity in properties. Wislicenus had isolated from meat-extract a lactic acid which was not identical with Scheele's well-known substance, but the difference was not so marked as was to be anticipated in the case of an isomeride such as the theory predicted. The effort to ascertain, by synthetic methods, the constitution of the two acids proved exceedingly difficult, the products being mixtures of several substances of which ordinary lactic acid certainly appeared to be the main constituent. Finally, a third distinct compound having the composition of a lactic acid was discovered by Beilstein; in regard to this latter substance, however, its recognition as a third isomeride was greatly delayed by an unfortunate mistake on the part of its discoverer. The discovery, in fact, increased instead of simplifying the complexity of the question.

At the present time, having the key in our possession, we are able to trace without difficulty the structural relationship of these acids

which, to those workers, was obscured by masses of detail. These details are now of secondary importance. They serve, however, to make clear to us the way in which the first suspicions in the mind of Wislicenus were aroused.

Even when surmise became conviction, it would not have been characteristic of his judicial intellect had he altogether discarded the theories which he perceived to be in the main so fruitful and so nearly accurate. To him it was more natural to assume that the explanation might be found in some extension of these theories, and with brilliant discernment he showed the precise direction in which that extension was to be made, namely, by taking into account the arrangement of the various parts of the molecule in tridimensional space, and he even attempted to represent such a conception in a graphic manner.

His views were expressed in his address to the Naturforscherversammlung at Innsbruck in 1869, and shortly afterwards he gave them a wider publicity in the new *Berichte der deutschen chemischen Gesellchaft*[1] in connection with a paper on the modifications of lactic acid. The precise words he employed are worthy of quotation. "Tatsachen wie diese werden dazu zwingen die Verschiedenheit isomerer Molecüle von gleicher Structurformel durch verschiedene Lagerung ihrer Atome in Raum zu erklaren und sich nach bestimmten Vorstellungen daruber umzusehen."

The new shoot which was thus grafted on the stock of structural chemistry did not at once show signs of growth, although it was imperceptibly acquiring vitality as the external conditions were becoming more suited to its free development.

It was at Zürich, also, that Wislicenus interested himself for a time in the question of the origin of muscular energy, his association with his friend and colleague Adolf Fick being doubtless responsible for his temporary divergence in this direction.

At that time Liebig's theory held the field, it being generally supposed that the energy necessary for muscular power was furnished by the combustion of the muscle-substances, that is to say, of nitrogenous albuminous materials, whilst that supplied by the oxidation of the carbohydrates and fats was mainly of use in maintaining the temperature of the body. This theory did not commend itself to Fick and Wislicenus, and on August 30, 1865, they undertook the ascent of the Faulhorn, near Interlaken, for the purpose of obtaining direct experimental evidence on the point. The minimum work done in the ascent was easily calculated, whilst the amount of nitrogen in the urine voided during the journey supplied the basis for computing that part of expended energy which was supplied by the destruction of the muscle-material, a computation which subsequent experiments

[1] 1869, 2, 620.

of Frankland rendered even more simple. The results indicated that the nitrogenous constituents were responsible only for a certain part of the energy expended, and the later investigations of Voit, Pettenkofer, and others have entirely confirmed this conclusion.

In 1872 Wislicenus was invited to succeed Adolf Strecker at Würzburg, and the move must have been congenial to him, for it brought him closely into contact with a number of men of intellect, including Kohlrausch, von Wagner, Sachs, and Sandberger. Here his attention turned more particularly to problems of a nature suited to the powers of the numerous young workers whose studies he was called on to direct. From his fertile imagination fell the ideas which were the starting points of many fruitful and varied experimental investigations. In particular, the syntheses with the aid of molecular silver, and those involving the use of acetoacetic or malonic ester, led to the development of fields in which his students found abundant space for useful work. The extraordinary volume and the importance of the new observations which flowed from his laboratories during this period evoked the admiration of the scientific world.

The time and attention which his synthetic researches claimed left Wislicenus few opportunities for other investigations, and the development of the conception of space configuration and its influence on isomerism was making but little progress, at least on the practical side. In the interval, however, the theoretical foundation on which is based our present view of stereochemical relationships among carbon compounds had been laid by van't Hoff and Le Bel. "La Chemie dans l'Espace," van't Hoff's famous thesis, appeared in 1875, and it is not to be doubted that Wislicenus, perhaps more clearly than any other chemist, foresaw at once the vast fields of research which the new theory was to open up. At his desire, a German edition of van't Hoff's work was undertaken by Felix Hermann. This appeared in 1877 under the title "Die Lagerung der Atome im Raume," and contained the matter of the French edition together with a preface by Wislicenus himself, who did not rest with this effort to make the new hypothesis familiar to a wide circle, but took every available opportunity to press its merits on the chemical world, which was disposed to accord it a cold reception, and, in some quarters, even to greet it with derision.

The death of Kolbe, the most uncompromising opponent of "chemistry in space," left vacant the Chair of Chemistry at Leipzig, and the University was set the difficult task of finding the man most fitted to take his place. The great, and perhaps not unexpected, honour fell to Wislicenus, and in 1885 he entered on his new duties, which he continued to discharge until his death two years ago.

At Leipzig, Wislicenus was at last able to give his whole mind to

the question of the space distribution of the molecule, the first definite step forward being found in a paper to the Königl. Sächs. Gesellschaft der Wissenschaften in 1887.[1] This paper was entitled "Ueber die räumliche Anordnung der Atome in organischen Moleculen und ihre Bestimmung in geometrischisomeren Verbindungen," and was based on van't Hoff's conception of the analogy between a carbon atom and a regular tetrahedron, but involved considerations of a chemical nature on which van't Hoff had barely touched. The mutual attractive or repulsive forces of the groups attached to adjacent carbon atoms were considered in connection with the relative positions which these atoms, when only singly bound to one another, would be likely to adopt.

The history of his subsequent investigations in this field is so recent and generally so well known that I may leave the details for later discussion, since it is impossible in a few words to convey an adequate impression of the services which they rendered to the science of stereochemistry.

Turning for a while to Wislicenus in the *rôle* of teacher, it may be at once asserted that his claim to our grateful recollection is of the highest. He was endowed with all the qualifications which should form the real basis of a great teacher, and on that foundation he built with scrupulous care, and the words he used in speaking of his old master Heintz applied not less truly to himself: "Wie der Forschertätigkeit, so war ihm auch sein Lehramt und der Umgang mit der Jugend Hertzensache."

Doubtless to the beginner and to young medical students the matter of his lectures must have seemed somewhat tough, but his hearers, one and all, were impressed by his lucidity and by the lively and interesting way in which he presented the material he handled. The feeling that the lecturer was thoroughly at home in all departments of his subject quickly won the confidence of every audience which he addressed.

In the laboratory he was equally conscientious and successful. Everyone there, down to the youngest worker, was personally known to him. By the careful questions he put, he aroused their pride in making accurate observations, and urged them to think and investigate for themselves, thus awakening their interest and developing their skill. He found the way to imbue those who worked under him with something of his own persistence, so that, in spite of experimental difficulties or long series of reverses, they came to regard the abandonment of a piece of work as an idea not to be entertained.

Discussions with his pupils were a source of real pleasure to

[1] Wislicenus gave the substance of this paper in a lecture to Section *B.* at the meeting of the British Association in Manchester in 1887.

Wislicenus, and by founding the Chemical Societies of Zürich, Würzburg, and Leipzig, of which he was always the life and soul, he aimed to bring students and staff more closely into contact, and thus simultaneously to strengthen their desire to acquire a wide knowledge and to increase their interest in research work. It is perhaps not too much to say that the intellectual development of young chemists was to Wislicenus a study as absorbing as any of his chemical problems.

Many of us must recall with pleasure the weekly meetings at which Wislicenus gathered his students round him at his simple mid-day meal. His house was open to students and friends of all ages and positions, and here, as well as at the annual "Bierfrühschoppen," where he entertained his colleagues and pupils, the genial and kindly nature of their host was patent to all.

Those of us who shared these privileges are not likely to forget the impression produced by his personality. His long beard, his fine head with its intellectual features, and his majestic carriage aided in producing a sensation which in younger men was not far from veneration.

The warm feelings entertained towards him by his students doubtless gave him keen pleasure, but formal tokens were always distasteful to him. At the approach of his sixtieth birthday it came to his ears that covert preparations were on foot to give special recognition to the occasion, and the distress which he showed was so evidently sincere that nothing remained but to abandon any idea of celebration.

To his love for teaching may be traced the reappearance of Strecker's text-book, originally based on Regnault's "Premiers Eléments de Chemie." After the death of Strecker in 1871, Wislicenus took upon himself the task of rewriting this book, which involved him in many years' work. In 1874 the organic portion was published (sixth edition), but the inorganic portion (ninth edition) did not make its appearance until 1887; both were in reality new works, for during the years which intervened the condition of chemistry had undergone a complete transformation.

If to the task of carrying on his scientific work and to the guidance of his pupils he devoted most scrupulous care, he was not less punctilious in the fulfilment of other duties which fell in no short measure on his shoulders. Of his professorial functions one of the least agreeable was that of examining, but the irritation which an examination entailed on him did not affect the sincerity of his efforts to form a just estimate of the men who came before him.

His colleagues have borne eloquent testimony that his thorough grasp of detail as well as principle was noticed in all his dealings with the faculty of his University. Seldom was he absent from a business meeting, and it was not often that an important question was mooted on which he had not some illuminating suggestion to make. His

advisory reports were always constructed with great care, and were clear and finished. In addition to the duties of his chair, he found time in Leipzig to fill the offices of Dean and Rector magnificus, positions to which, as was generally conceded, he brought exceptional dignity. Twice in Würzburg he was honoured by a call to the Rector's seat, and on the second occasion the summons implied more than ordinary confidence in the man selected, for the tenure of office was intended to cover the celebrations in commemoration of the 300th year of the University's existence.

In spite of the extraordinary calls which his acadamic and scientific work made on his energy, he still was able to take a prominent part in political affairs. So far as was possible, he held himself aloof from party strife, and for this reason he staunchly resisted all proposals that he should submit himself for election to the Reichstag, and only consented with reluctance to take office as a town-councillor at Leipzig. But when the call came to fight for large ideals and for the future of the German people, the instincts of the leader always brought him to the front.

Wislicenus was a German to the core. At school the German language was one of his hobbies, and the folk-lore and mythology of his country were an absorbing study. His long exile in other lands only served to strengthen his patriotism, and he followed heart and soul the efforts of his countrymen to form a united nation. He was an ardent follower of Bismarck, and never hesitated to give the freest expression to his opinions. He strove constantly to promote a German colonial policy, and was a keen advocate of proposals to form a great German navy. Nevertheless throughout his life he kept a warm place in his heart for Switzerland, his foster-mother.

An incident which illustrates some of the prominent features in the character of Wislicenus may be related. Shortly after the conclusion of peace between France and Germany, a gathering of the German inhabitants of Zürich was held to celebrate the occasion, and Wislicenus was nominated chairman. The Francophile portion of the population attacked the meeting hall with stones, and set fire to the staircase. A panic arose among the merry-makers, but Wislicenus, with a well-timed appeal to their patriotism, restored their confidence, and then proceeded, with the utmost coolness, to show them how defences might be formed, and to extinguish the burning stairs with beer.

He left the hall immediately afterwards, and walked quietly through the mass of excited people whose intention it had been to stone him. But his commanding presence at once put a stop to any such idea, and no one ventured to assault him.

Shortly after he settled in Zürich, Wislicenus married Katherine

Sattler, the grand-daughter of Wilhelm Sattler, of Schweinfurt, who shared with Russ the discovery of "Schweinfurt green." His happiness was not long unmarred by misfortune, for in 1866, Hugo, his brother, who at the time was Privat-docent in the Faculty of Germanic Archæology at Zürich, lost his life as the result of an accident in the Alps. This blow was followed by others even more severe. His wife, after ten cloudless years, was seized with an incurable mental disorder, and two gifted sons were taken from him before attaining manhood. The marks made by these calamities were never effaced, but the interest which he took in his fellow men was not thereby lessened. He sought to save his friends distress by striving to conceal his pain, and it is more than likely that the restraint which he thus imposed on himself started the first tremor which finally led to the breakdown of his overburdened frame.

His two remaining sons followed in their father's footsteps, and he was able to rejoice in their successes. Of his two daughters, the elder, Emilie, remained with him until his death, sharing his joys and troubles; his second daughter, Marie, lived in Zürich after her marriage, and in later years father and daughters met there at frequent intervals. The relations between Wislicenus and his children were ideal, and the sympathy which bound the household can fully be realised only by those who have had the privilege of entering the family circle. Holidays, to them, meant the fields and woods. The father had built a charming country house in the Schonungen district, not far from Schweinfurt, and there, in the peaceful valley below the picturesque fortress of Mainberg, he spent a part of his vacations in quiet study, or sought to gain new energy by tramping the woods with gun on shoulder and his mind full of the interests of country life.

I may now be permitted to review in greater detail some of the scientific work associated with the name of Johannes Wislicenus. At the commencement of his career, the study of organic chemistry had greatly weakened the hold of the Berzelius dualistic electrochemical theory, at least as a universal principle, for the direct application of that conception to carbon compounds had proved fruitless, and it was beginning to be felt that even the "radical" theory of Liebig and Dumas would prove inadequate. A brilliant procession of new and unexpected observations was passing before the eyes of the chemical world, and the revolutionary ideas of Gerhardt were attracting the fancies of the younger schools of chemists, although, as is usually the case when doctrines of tried utility are threatened by overthrow, the new views were opposed by several of the elder men.

It was entirely in accordance with the independence of thought which his judgment so often displayed that, in his first contribution to chemical literature, of which mention has already been made, Wislicenus dissociated himself from the conservatism of his teacher, Heintz, and proclaimed himself an adherent of the new principles. Simultaneously with this theoretical paper on glycerine and the polyatomic alcohols appeared others in which was detailed the experimental basis for the conclusions drawn, the principle that theory and experiment must yield each other mutual support being his guide throughout his scientific career.

When Wislicenus resumed work at Zürich, the problem of the constitution of lactic acid was in the air. The discovery of glycol by Würtz in 1856, and the publication of Heintz's synthesis of glycollic acid from chloracetic acid, had paved the way for a preliminary agreement between the schools of Würtz and Kolbe. The former saw in lactic acid a "diatomic radical, $C_3H_4O_3$"; the latter based his views on the broader conception that the substance was really a monobasic acid, and endeavoured to show that it was very simply derived from propionic acid, which he conceived as "ethyl formic" acid; to lactic acid he, therefore, attributed the functions of a "(hydr)oxyethyl formic" acid, and, in the older symbols to which he permanently adhered, he expressed its structure by the type formula $HO\left(C\left\{\begin{matrix}H\\HO_2\end{matrix}\right.\right)[C_2O_2],O$.

Wislicenus entered the field without preformed notions, and, recognising that the difference of opinion arose largely as the result of too narrow conceptions of the type theory, endeavoured to show that it was easy, merely by extending the idea of radicles within radicles, to express all that was then known as to the behaviour of lactic acid. He emphasised the fact that, in accordance with Kolbe's view, lactic acid is monobasic, and that the *second* replaceable hydrogen atom has the same character as the replaceable hydrogen in alcohols.[1] The *di*sodium derivative of lactic acid behaves in much the same manner as does an alcoholate, being decomposed by carbon dioxide, and even by water, into the *mono*sodium derivative and sodium carbonate or hydroxide, whilst the formation of a sodium derivative of ethyl lactate is in accordance with the belief that this ester still retains an alcoholic function. He considered, in the terms then in vogue, that the divalent carbonyl radicle is "neutralised" on one side by union with a positive, univalent alcohol radicle, leaving it negatively univalent, whilst in the alcohol radicle itself there is also the hydrogen atom, which is replaceable by acid groups and capable of being removed with the oxygen atom in exchange for an atom of chlorine.

[1] *Annalen*, 1863, **125**, 41—70.

The formula he employed to crystallise his view of lactic acid was

$$\left.\begin{array}{c} CO'' \\ \left.\begin{array}{r} C_2H_4 \\ H \end{array}\right\} O \\ H \end{array}\right\} O,$$

and he indicated how clearly this accounted for the isomerism of the two methyl derivatives:

$$\left.\begin{array}{c} CO'' \\ \left.\begin{array}{r} C_2H_4 \\ CH_3 \end{array}\right\} O \\ H \end{array}\right\} O \quad \text{and} \quad \left.\begin{array}{c} CO'' \\ \left.\begin{array}{r} C_2H_4 \\ H \end{array}\right\} O \\ CH_3 \end{array}\right\} O,$$

and by hydrolysing Perkin's ethyl acetyl-lactate he succeeded in isolating acetyl-lactic acid and its salts:

$$\left.\begin{array}{c} CO'' \\ \left.\begin{array}{r} C_2H_4 \\ C_2H_3O \end{array}\right\} O \\ C_2H_5 \end{array}\right\} O \qquad \left.\begin{array}{c} CO'' \\ \left.\begin{array}{r} C_2H_4 \\ C_2H_3O \end{array}\right\} O \\ H \end{array}\right\} O$$

Ethyl acetyl-lactate. Acetyl-lactic acid.

He went on, shortly after this, to the study of malic, tartaric, citric, and mucic acids,[1] to which similar views appeared to be capable of application. These acids were generally recognised to be dibasic in character, and Kekulé regarded malic acid, for example, as a "triatomic dibasic" acid, whilst Kolbe preferred to picture it as a "dibasic mono(hydr)oxy" acid. In order to determine how far the additional oxygen atoms in these acids correspond in function with the third oxygen atom in lactic acid, Wislicenus investigated the action of acetyl chloride on their neutral esters, the conclusions which he was able to draw being, (1) that the so-called atomicity of an acid is the sum of the positive hydrogen atoms which are easily replaceable by metals or alcohol radicles and of the negative hydrogen atoms which are replaceable by acid radicles; (2) that the number of the negative hydrogen atoms of the second type is best determined by the action of acetyl chloride on the neutral esters.

While dealing with his conception of the univalent radicle $\left.\begin{array}{r} C_2H_4 \\ H \end{array}\right\}' O$ in his lactic acid formula, he pointed out that such a radicle is existent in glycolmonochlorhydrin, $\left.\begin{array}{c} \left.\begin{array}{r} C_2H_4 \\ H \end{array}\right\}' O \\ Cl \end{array}\right\}$, and other glycol compounds.[2] He endeavoured to replace the halogen atom in glycolmonochlorhydrin by the cyano-group through the agency of potassium cyanide, and by hydrolysis of the product to convert the compound

[1] *Annalen*, 1864, **129**, 175—200. [2] *Ibid.*, 1867, **128**, 1—67.

into one of the carboxylic type. The method afforded him an acid having the formula $C_3H_6O_3$, which at the time he considered in all probability to be paralactic acid (now known as α-hydroxypropionic acid), trusting to observations on the properties of its zinc salt for the evidence as to its identity. It must be said, however, that subsequent experiments of Erlenmeyer[1] proved that the conclusion drawn by Wislicenus was erroneous, for the acid obtained from glycolchlorhydrin by the above mode of treatment yields the characteristic zinc-calcium salt of hydracrylic acid (or β-hydroxypropionic acid); Erlenmeyer also showed that this method gives but a poor yield of the synthetic product, which is more easily obtained if the intermediate ethylene cyanohydrin be prepared by leaving together a mixture of ethylene oxide and hydrocyanic acid.

The existence of a genetic relationship between acetaldehyde and lactic acid proper had been rendered probable by Staedler and by Engelhardt among others, for aldehyde could be obtained from the acid in several different ways; Strecker, moreover, had effected a synthesis of lactic acid from acetaldehyde by way of alanine (α-aminopropionic acid). These facts suggested to Wislicenus that the divalent radicle, C_2H_4'', of ordinary lactic acid was identical with the "ethylidene" radicle of acetaldehyde, and he confirmed this suggestion experimentally by a synthesis of lactic acid from the aldehyde—a synthesis which was analogous, at least in appearance, to that by means of which glycolchlorhydrin had yielded him the isomeric acid. The process consisted in preparing the requisite ethylidenechlorhydrin by the direct addition of hydrogen chloride to aldehyde, and subjecting the halogen compound to the usual processes; he also effected the synthesis by the now well-known method involving the formation of ethylidenecyanohydrin by direct addition of hydrogen cyanide to the aldehyde.

At this juncture he considered the results of experiments to justify the conclusion that the existence of two isomeric C_2H_4'' radicles in paralactic acid from meat juice and ordinary lactic acid respectively was established; in the paper appear for the first time the names "ethylenelactic acid" and "ethylidenelactic acid," and these terms have remained in common use up to the present time, although the error made by Wislicenus in the application of the former term to paralactic acid was soon corrected when Erlenmeyer showed that hydracrylic acid was the compound to which it should properly be assigned.

In the same paper which contains the account of these results[2] is to be found an interesting discussion on different modes in which the reactions of lactic acid could be expressed by type-theory formulæ, and a free translation of the concluding remarks on this subject may be

[1] *Annalen*, 1867, **141**, 261. [2] *Ibid.*, 1863, **128**, 1 *et seq.*

given. "The formulæ for lactic acid, which I have given above, represent, not different, but one and the same kind of combination between the parts of the lactic acid molecule; the radicles in them are identical, the kind of mutual saturation is the same throughout, and the only change made is the order in which they come. Such a change in order would always be justified even if we understood the mode in which the atoms are distributed in space, because our present formulæ can do no more than present us with a picture of the compound in one plane. If we wish to represent the properties of a compound from all points of view, many different formulæ, emphasising different characteristics, are necessary, and so long as these different chemical formulæ exhibit the differences in order only and not in the type of union of the adjacent parts, so long, in my opinion, will they be wanting in scientific precision." He here seized the opportunity to point out that the theory of molecular structure must be set on a broader basis, remarking that it was no longer possible to contend that the equivalent substitution of hydrogen produces only secondary effects on the general character of a compound.

The properties of the so-called "anhydrous lactic acid" next absorbed his energies.[1] Pelouze had investigated the action of ammonia on this substance, and found that ammonium lactate was formed, whilst Laurent found that only one-half of the ammonia absorbed could again be directly obtained in the form of platinichloride, the other half being combined in a non-separable form. Laurent drew the conclusion that the product he obtained arose as the result of a decomposition of an ammonium aminolactate or lactamate, Wislicenus[2] had already suggested that "anhydrous lactic acid" was ester-like in character, one residue of lactic acid functionating as the acid radicle and another as the alcoholic radicle, so that by the action of ammonia it might be expected to afford one molecule of lactamide and another of lactic acid, or rather of its ammonium salt; by carrying out the reaction with ammonia in an alcoholic solution of "anhydrous lactic acid," he was able to prove that both these compounds are formed immediately, and therefore are not merely secondary products as Laurent had supposed.

During the next two or three years a great advance was made, because Frankland's graphic methods of representing the constitution of carbon compounds began generally to be adopted, and we find them employed in all the subsequent communications from Wislicenus on the subject of lactic acid, hence it will not be inconsistent if at this point I follow the sequence of historical events, and at once employ the modern graphic symbols to depict the process by which Brügger, in 1864, confirmed the views of

[1] *Annalen*, 1865, **133**, 257. [2] *Ibid.*, 1863, **128**, 60.

Wislicenus regarding the nature of "anhydrous lactic acid," or "dihydrolactic acid," as it has more recently been termed. Brügger's method [1] consisted in heating potassium lactate with α-bromopropionic acid, the product proving to be the anhydro-compound in question.

$$\begin{array}{l} CH_3 \\ | \\ CH(OH) \\ | \\ CO{\cdot}OK \end{array} + \begin{array}{l} CH_3 \\ | \\ BrCH \\ | \\ CO{\cdot}OH \end{array} = \begin{array}{l} CH_3 \\ | \\ CH(OH) \\ | \\ CO{\cdot}O \end{array} \begin{array}{l} CH_3 \\ | \\ CH \\ | \\ CO{\cdot}OH \end{array} + KBr.$$

A striking observation of Strecker's arrested the attention of Wislicenus; by the action of heat on sarcolactic acid, an anhydride of ordinary lactic acid was obtained, and Wislicenus, who at this time considered that sarcolactic or paralactic acid was ethylenelactic acid, supposed that this involved a conversion of β-hydroxypropionic acid into α-hydroxypropionic acid, and in order to determine if such a change might be brought about in the homologues of lactic acid, he examined the properties of the hydroxybutyric acid which he prepared for the purpose by the reduction of Geuther's acetylacetic ether. This acid he considered to be the analogue of paralactic acid, for the isomeric acid prepared by Friedel and Machucca from brominated butyric acid he correctly supposed to be the corresponding α-hydroxy-acid. He was unable to satisfy himself that, on heating β-hydroxybutyric acid, any change took place corresponding with that noticed by Strecker in the case of paralactic acid, but observing that the salts of β-hydroxybutyric acid swelled when heated, he suggested that the non-occurrence of the expected isomeric change was the result of the conversion of the compound into the unsaturated acid by loss of a molecule of water.[2] It is now clear, of course, that the change which paralactic acid undergoes when heated is a simple case of racemisation, such as occurs also in the case of mandelic acid, involving no further structural alteration.

It was at about this time that his first important paper on the acid from β-iodopropionic acid made its appearance.[3] Beilstein had previously carried out the hydrolysis of the iodo-acid by moist silver oxide, but, unfortunately, had failed to recognise the true character of the product, to which he assigned the name "hydracrylic acid" and the formula $C_{12}H_{22}O_{11}$. Two years afterwards, Moldenhauer found that Beilstein's acid could be converted into a compound having the same empirical formula as lactic acid by heating it with a solution of alkaline hydroxides, and this paper was succeeded by others emanating from Wichelhaus and from von Richter. Wislicenus re-examined Beilstein's acid, and, by preparing its crystalline salts, succeeded in proving that

[1] *Zeit. für Chem.*, 1869, **5**, 338.

[2] *Annalen*, 1869, **149**, 205—215.

[3] *Zeit. für Chem.*, 1868, **4**, 683—684.

it was isomeric with lactic acid. He returned to the subject some years later[1] in consequence of an expression of opinion from Wichelhaus, who considered that hydracrylic acid was identical with ethylenelactic acid; an opinion which Wislicenus did not share, although, as he believed, ethylenelactic acid is undoubtedly present in small quantities in the crude acid from meat-extract. It is only fair to note that both Erlenmeyer and Klimenko failed to confirm the latter statement. Wislicenus showed that the action of silver oxide on β-iodopropionic acid affords, not only a lactic acid, but also acrylic acid, $C_3H_4O_2$, and two isomeric acids having the formula $C_6H_{10}O_5$. which he termed dehydracrylic and paradipimalic acids respectively. Heintz, by warming β-iodopropionic acid with milk of lime, also observed the formation of lactic and acrylic acids, but did not detect the other acids discovered by Wislicenus; he also discovered the characteristic double zinc-calcium salt of the lactic acid formed. Heintz, like Wichelhaus, believed that Beilstein's acid must be regarded as ethylenelactic acid.

The reason urged by Wislicenus in support of his contention that hydracrylic acid is not ethylenelatic acid was that he was unable to convert it into malonic acid, which the latter afforded him without difficulty; moreover, the acid which he had obtained from ethylene-chlorohydrin had refused to yield β-iodopropionic acid on treatment with hydrogen iodide, and gave only amorphous salts, whilst hydracrylic acid could be reconverted into β-iodopropionic acid without difficulty.

He considered that the two compounds were very closely related, however, and suggested that β-iodopropionic, glyceric, hydracrylic and acrylic acids were not true carboxylic acids, and his conception of their relationship was expressed by the following formulæ:—

$CH_2{\cdot}I$	$CH_2{\cdot}OH$	$CH_2{\cdot}OH$	CH_2
$\vert$	$\vert$	$\vert$	$\Vert$
$O<\begin{array}{l}CH\\ \vert\\ CH{\cdot}OH\end{array}$	$O<\begin{array}{l}C{\cdot}OH\\ \vert\\ CH{\cdot}OH\end{array}$	$O<\begin{array}{l}CH\\ \vert\\ CH{\cdot}OH\end{array}$	$O<\begin{array}{l}CH\\ \vert\\ CH{\cdot}OH\end{array}$
β-Iodopropionic acid.	Glyceric acid.	Hydracrylic acid.	Acrylic acid.

It was the experiments of Erlenmeyer,[2] to which reference has already been made, which revealed the trap into which Wislicenus had fallen, and served to establish the identity of hydracrylic and ethylene-lactic acids.

Wislicenus, in 1873, once more took up the investigation of the acids from meat-extract,[3] and confirmed Strecker's observation that para-lactic acid may be converted into the anhydride of ordinary lactic acid,

[1] *Annalen*, 1873, **166**, 3, *et seq.* [2] *Ibid.*, 1878, **191**, 261.
[3] *Ibid.*, 1873, **166**, 3—64; **167**, 302—346.

and proved that, by heating the former at 135—140°, a complete conversion of the active into the inactive acid may be brought about. Comparative experiments on the two acids showed him that both compounds yield aldehyde and under precisely similar conditions, forcing him to the conclusion that there is no profound difference in structure between the two, so that the facts accumulated up to that time indicated clearly enough that paralactic acid and fermentation lactic acid must be represented by the same chemical formula,

$$\begin{array}{l} CH_3 \\ | \\ CH{\cdot}OH. \\ | \\ CO_2H \end{array}$$

It is worth while to quote the words in which he announced his conclusion to the German Chemical Society,[1] for they must be memorable as marking the first step towards the development of chemistry in space. "Es ist damit der erste sicher constatierte Fall gegeben, dass die Zahl der Isomeren die der Struckturmöglichkeiten übersteigen kann. Tatsachen wie diese werden dazu zwingen, die Verschiedenheit isomerer Molecüle von gleicher Strucktur formel durch verschiedene Lagerung ihrer Atome im Raum zu erklären und sich nach bestimmten Vorstellungen darüber umzusehen."

For the type of isomerism which depends on the varying space distribution of the atoms in the molecule, he used the term "geometrical isomerism,"[2] a name which was afterwards replaced in 1888 by the word "stereoisomerism," coined by Victor Meyer.

The years over which the investigations on lactic acid extended were not without results in other fields. At one time Wislicenus seems to have taken some interest in inorganic chemistry and in water and gas analysis, but this was in his earlier years, and his later work lay almost exclusively in the domain of carbon chemistry.

In 1869 appeared his first paper on the subject of the dibasic acids of the oxalic series $C_nH_{2n}(CO_2H)_2$.[3] The nomenclature which he here proposed for the first few members of the series is practically the same as that in use at the present time, except that "lipic acid" has become "glutaric acid." In this communication the use of "molecular silver" as a synthetic agent is described for the first time; this agent, prepared by the reduction of silver chloride in the cold, was heated with β-iodopropionic acid, first at 100—120°, and then at 150—160°, the product being adipic acid,

$$2CO_2H{\cdot}CH_2{\cdot}CH_2{\cdot}I + 2Ag = \begin{array}{l} CH_2{\cdot}CH_2{\cdot}CO_2H \\ | \\ CH_2{\cdot}CH_2{\cdot}CO_2H \end{array} + 2AgI.$$

[1] *Ber.*, 1869, **2**, 620. [2] *Annalen*, 1873, **167**, 345.
[3] *Ibid.*, 1869, **149**, 215—224.

A synthesis of another member of this series, namely, succinic acid, was also accomplished, and this experiment appears to have given rise to the long and valuable series of researches on acetoacetic ester which emanated from the laboratories of Zürich and Würzburg under the auspices of Wislicenus. The synthesis referred to consisted in bringing ethyl chloroacetate into reaction with the product obtained by the action of sodium on ethyl acetate—a product which was generally held to be a simple substitution derivative, although Geuther himself maintained the view which is now known to be the correct one. The conception which, at the time, Wislicenus formed of the process was as follows :—

$$Cl{\cdot}CH_2{\cdot}CO_2{\cdot}C_2H_5 + Na{\cdot}CH_2{\cdot}CO_2{\cdot}C_2H_5 = \begin{matrix} CH_2{\cdot}CO_2{\cdot}C_2H_5 \\ | \\ CH_2{\cdot}CO_2{\cdot}C_2H_5 \end{matrix} + NaCl.$$

The method was found to lead to the formation of a by-product, the investigation of which Wislicenus left in the hands of his pupil Noeldecke, who succeeded in proving it to be acetopropionic acid, $CH_3{\cdot}CO{\cdot}CH_2{\cdot}CH_2{\cdot}CO_2H$; this substance, as was afterwards shown, is produced by the elimination of carbon dioxide from acetosuccinic acid, from the ethyl ester of which in reality the succinic acid formed in the reaction is also produced.

In the same year appeared communications on duplothioacetone,[1] which he prepared from acetone by means of phosphorus trisulphide, and on the dibromobenzenes. His investigations on the latter subject were carried out in conjunction with Riese, and included experiments on the action of sodium on the crystalline dibromo-compound, a process which gave rise to diphenyl, diphenylbenzene, and other products; the oily "β-dibromobenzene" which accompanies the former was purified and converted into its nitro-derivative, and the latter shown to be different from the nitro-compound of crystalline dibromobenzene.

Among the first papers published by Wislicenus after his promotion to Würzburg was a communication on a synthesis of hydantoic acid, which was shown to be the product obtained when cyanic acid acts on glycocoll.[2]

$$\begin{matrix} CH_2{\cdot}NH_2 \\ | \\ CO_2H \end{matrix} + HCNO = \begin{matrix} CH_2{\cdot}NH{\cdot}CO{\cdot}NH_2 \\ | \\ CO_2H \end{matrix}.$$

The synthesis of ethylmalonic acid from normal butyric acid was accomplished by him in conjunction with Urech,[3] the process involving the conversion of the butyric acid into its α-brominated derivative, which, by the action of potassium cyanide, followed by

[1] *Zeit. für Chem.*, 1869, 5, 324—326. [2] *Annalen*, 1873, 165, 103.
[3] *Ibid.* 93—98

the hydrolysis of the resulting α-cyanobutyric acid, gave the substituted malonic acid without difficulty,

$$CH_3{\cdot}CH_2{\cdot}CHBr{\cdot}CO_2H \longrightarrow CH_3{\cdot}CH_2{\cdot}CH(CN){\cdot}CO_2H \longrightarrow CH_3{\cdot}CH_2{\cdot}CH(CO_2H)_2.$$

The years 1874 and 1875 were signalised by the appearance of a long series of communications from the Würzburg laboratories.[1] These were mainly the results of work undertaken by his students, and covered a very wide range. With Goldenberg, benzoin was shown to be capable of reduction to Zinin's desoxybenzoin, and the latter to dibenzyl, while benzoinpinacone was obtained for the first time. Bonné, Goldenberg, and Zimmermann investigated silver derivatives of biuret and its allies, and used them to prepare alkyl derivatives. To Zimmermann was entrusted an interesting piece of work on the constitution of phosphorous acid, the possibility that triethyl phosphite might be represented by the formula $O{:}P{\lt}^{C_2H_5}_{O{\cdot}C_2H_5}{}_{O{\cdot}C_2H_5}$ being tested and disposed of by showing that the ester yields no ethylphosphinic acid on hydrolysis, but only phosphorous acid, and that by absorption of oxygen it is converted into ethyl phosphate, $O{:}P(O{\cdot}C_2H_5)_3$; it was also observed that, on addition of sodium hydroxide to concentrated phosphorous acid, a syrup may be obtained in which the ratio P : Na is approximately 1 : 3, the conclusion being drawn that $P(OH)_3$ correctly represents the properties of the acid.

The investigation of the behaviour of zinc ethyl towards dichloroether fell into the hands of Kessel, and Frankland's "dinitroethylic acid" gave Zuckschwerdt results which appeared to Wislicenus to justify the formula $O{\lt}^{N{\cdot}C_2H_5}_{N{\cdot}C_2H_5}$ (the two N atoms joined) for that compound. Zuckschwerdt, also re-examined the complex product obtained when sulphur dioxide is brought into contact with zinc ethyl.

A useful synthetic process was worked out by Forster, who found that mercuriphenylammonium chloride reacts smoothly with thiocarbamides, the process leading to the production of guanidines,

$$NHg(C_6H_5)HCl + S{:}C(NHC_6H_5)_2 = HgS + N(C_6H_5){:}C(NH{\cdot}C_6H_5)_2,HCl.$$

The study of the isomeric solid and liquid crotonic acids was undertaken by V. Hemilian; the pure solid acid gave both "α" and "β" sulpho- and iodobutyric acids, a fact which led Wislicenus to conclude that the formula $CH_3{\cdot}CH{:}CH{\cdot}CO_2H$ represented the struc-

[1] *Ber.*, 1874, **7**, 286—298, 683—692, 892—893; 1875, **8**, 1034—1040, 1206—1209.

ture of solid crotonic acid, whilst the liquid acid was presumably $CH_2{:}CH{\cdot}CH_2{\cdot}CO_2H$, although, as he admitted, malonic acid is not among the products formed when the liquid acid is fused with potassium hydroxide. This communication is of especial interest when it is remembered that the difference between the two acids was afterwards assigned by Wislicenus to stereochemical causes, the existence of which he was at this time being led to infer from his lactic acid researches.

In the same set of papers is one containing an account of the work which initiated the long series of syntheses by the aid of pure acetoacetic ester which were carried out in the Würzburg laboratories.[1] Wislicenus cited here the new evidence confirming Geuther's views and refuting the suggestions of others that the metal compound obtained by the action of sodium on ethyl acetate is a simple substitution derivative of the latter; the substance was definitely shown to be ethyl *sodio*acetoacetate, and attention was drawn to the improvement in the synthetic process which may be effected if, instead of employing the crude material prepared by heating ethyl acetate with sodium, the pure acetoacetic ester is first isolated; the use of benzene as a diluent and of excess of sodium, afterwards to be removed, was also suggested. Goldenberg, Ehrlich, Zeidler, Saur, and others carried out the experimental details of the work, proving that the product so prepared may afford nearly quantitative yields of substituted acetoacetic esters on treatment with alkyl iodides, benzyl chloride or benzoyl chloride. Finally, it was shown that the *mono*-substituted products are capable once more of reacting with sodium and alkyl iodides, affording the *di*-substituted derivatives, so that the complicated theories put forward by Frankland and Duppa and by Geuther in explanation of the production of dialkylacetic acids, as by-products in the old process, were rendered unnecessary.

With Conrad, whose name afterwards became so closely identified with the progress of the acetoacetic ester and malonic ester syntheses, Wislicenus was able satisfactorily to explain the origin of the dehydracetic acid which is formed by the distillation of acetoacetic ester, four molecules of which interact so that four molecules of ethyl acetate are eliminated,

$$4CH_3{\cdot}CO{\cdot}CH_2{\cdot}CO_2{\cdot}C_2H_5 = C_8H_8O_4 + 4CH_3{\cdot}CO_2{\cdot}C_2H_5,$$

whilst to Ruegheimer and Harrow is due the joint honour of the discovery of the synthetic reactions by which the sodium derivatives of β-ketonic acids may be converted into diacetylsuccinic esters,

$$2CH_3{\cdot}CO{\cdot}CHNa{\cdot}CO_2{\cdot}C_2H_5 + I_2 = \begin{matrix} CH_3{\cdot}CO{\cdot}CH{\cdot}CO_2{\cdot}C_2H_5 \\ | \\ CH_3{\cdot}CO{\cdot}CH{\cdot}CO_2{\cdot}C_2H_5 \end{matrix} + 2NaI.$$

[1] *Ber.*, 1874, **7**, 683.

Other papers published at this period, with Ehrlich, Rohrbeck, Waldschmidt, Saur, Conrad, and others as joint authors, dealt with the continuation of this work. The β-hydroxy-α-substituted butyric acids obtained as reduction products from the alkylacetoacetic esters came under observation, as well as the α-substituted crotonic acids which are produced by their dehydration; thus from methylacetoacetic ester, by this series of changes,

$$CH_3{\cdot}CO{\cdot}CH(CH_3){\cdot}CO_2{\cdot}C_2H_5 \longrightarrow CH_3{\cdot}CH(OH){\cdot}CH(CH_3){\cdot}CO_2H \longrightarrow CH_3{\cdot}CH{:}C(CH_3){\cdot}CO_2H.$$

a methylcrotonic acid was isolated and identified with the product prepared by Frankland and Duppa from ethomethoxalic acid, $CH_3{\cdot}CH_2{\cdot}C(CH_3)(OH){\cdot}CO_2H$, by removal of the elements of water. The hydrolysis of methylethylacetoacetic ester yielded a valeric acid which resembled ordinary valeric acid in nearly all particulars, except that its barium salt could not be obtained in a crystalline condition. With reference to this acid the remark is made, "aus dieser Synthese geht mit Sicherheit hervor, dass Erlenmeyer's Vermuthung der sogenannte optisch-active Amyl Alcohol entspreche der Formel $CH_3{\cdot}CH_2{\cdot}CH(CH_3){\cdot}CH_2{\cdot}OH$ und die daraus dargestellte Valeriansäure $CH_3{\cdot}CH_2{\cdot}CH(CH_3){\cdot}COOH$ in der That richtig sei," a conclusion which, although since proved to be correct, was perhaps scarcely justified by the results of the experiments just mentioned.

Arising out of the study of the action of sodium on ethyl acetate, an examination was made of the compound first isolated by von Fehling as the product of the action of sodium with ethyl succinate. Herrmann was instrumental in proving that the substance is similar in character to ethyl acetoacetate, but yields a mono- and also a di-potassium derivative decomposed by carbon dioxide, the results seeming at that time to indicate that the substance was a ring compound of the formula $\begin{array}{l}CH_2{\cdot}CO{\cdot}CH{\cdot}CO_2{\cdot}C_2H_5\\ |\qquad\quad\ |\\ CH_2{\cdot}CO{\cdot}CH{\cdot}CO_2{\cdot}C_2H_5\end{array}$.

The investigation of the isomeric ethylacetosuccinic esters Wislicenus assigned to Clowes and Huggenburg; the first of the isomerides was prepared by the interaction of ethyl sodioacetoacetate and ethyl α-bromobutyrate,

$$CHNa(CO{\cdot}CH_3){\cdot}CO_2{\cdot}C_2H_5 + CHBr(C_2H_5){\cdot}CO_2{\cdot}C_2H_5 = \begin{array}{l}CH(CO{\cdot}CH_3){\cdot}CO_2{\cdot}C_2H_5\\ |\\ CH(C_2H_5){\cdot}CO_2{\cdot}C_2H_5\end{array} + NaBr,$$

and the second by ethylating acetosuccinic ester,

$$\begin{array}{l}CHNa{\cdot}CO{\cdot}CH_3\\ |\\ CH_2{\cdot}CO_2{\cdot}C_2H_5\end{array} + C_2H_5I = \begin{array}{l}C(C_2H_5)(CO{\cdot}CH_3){\cdot}CO_2{\cdot}C_2H_5\\ |\\ CH_2{\cdot}CO_2{\cdot}C_2H_5\end{array} + NaI;$$

in accordance with the formulæ assigned, the former was attacked at once by sodium, hydrogen being evolved, whilst the latter was practically unaffected.

The most important communication from the pen of Wislicenus during the year 1877 was, without doubt, a masterly summary of the knowledge which had accumulated up to that time on the subject of ethyl acetoacetate and its applications as a synthetic agent.[1] In the following year this was supplemented by a valuable treatise on the manner in which the proportion of "acid" and "ketone" decompositions is regulated by varied conditions which may be imposed during the hydrolysis of the ester and its substitution derivatives,[2] the remarkable point elicited being the irregular modes in which the esters decompose and the consequent difficulty in foretelling even to a rough degree of approximation the way in which a new ester may behave under given circumstances.

It should be recorded that at about the period of which we are speaking, Conrad and Limpach, pupils of Wislicenus, worked out the details of the method, since then almost universally adopted in carrying out syntheses such as those involving the use of acetoacetic or malonic ester, namely, that of preparing the necessary sodium derivative by a process of double decomposition, the ester being added to alcohol in which the calculated quantity of sodium has previously been dissolved.

The work which Wislicenus entrusted to the author during his stay of two years (1880—1882) in Würzburg was the investigation of the condensation products which are formed when œnanthol is treated with caustic potash or other reagents, a subject which at that time was little understood, but which has since, in the case of other aldehydes, been thoroughly worked out by Lieben and his pupils. But in a laboratory like that of Würzburg, in which so much work of so varied a nature is being carried on, more, perhaps, is learnt by watching others than from the research the student is actually engaged in. The constant contact with men engaged in syntheses with the aid of ethyl sodioacetoacetate and sodiomalonate familiarised the author with these reagents and undoubtedly helped to suggest the methods which were subsequently employed in his researches on the formation of closed carbon chains. Indeed the first small experiment on the action of ethylene dibromide on the sodium compound of ethyl malonate was carried out in the Würzburg laboratories, but at that time without result.

The scientific papers associated with the name of Wislicenus between the years 1877 and 1887 are few in number; one or two dealing with compounds obtained by the acetoacetic ester synthesis, as well as others containing the results of experiments on dichloro-

[1] *Annalen*, 1877, **186**, 161—228. [2] *Ibid.*, 1878, **190**, 257—281.

ether and on reduction products of phthalic anhydride, are to be found, but these studies appear to have aroused in him only a passing interest. The work involved in the revision of Strecker's text-book, his academic and political duties, his translation to the Leipzig chair in 1885, were doubtless all in part responsible for the apparent falling off in importance of his contributions to chemical literature. The appearance in 1888 and 1889 of his epoch-making papers on space relations of the atoms in carbon compounds, on which he had pondered for many years, synchronised with a renewed activity in research work more commensurate with the expectations of the scientific world which knew his powers. From this time onwards his laboratory was the spring from which issued the stream of work which has helped to justify the use of those conceptions first foreshadowed by himself, and afterwards endowed with definite shape by the genius of van't Hoff.

Since the appearance of the original papers by Le Bel and van't Hoff, no serious attempt had been made to apply the theory to non-enantiomorphous isomerism, although van't Hoff had discussed the isomerism of compounds such as fumaric and maleïc acid in considerable detail. In order to explain the intraconversion of these two compounds, through the medium of the halogen derivatives of succinic acid, Wislicenus assumed that the groups on neighbouring carbon atoms act on one another in a manner determined by their "chemical affinities," and that in cases where these adjacent atoms are singly interbound, and hence doubtless free to rotate about the point of mutual attachment, such a rotation will take place as to lead to the adoption of the most favourable ("begünstigte") configuration. An arrangement so brought about would, he considered, be stable at low temperatures, but as the oscillations increased in violence with rise of temperature a new configuration might result.

In dealing with compounds of the type of fumaric and maleïc acids, and represented by the generalised formulæ

$$\begin{array}{c} a\cdot\mathrm{C}\cdot b \\ \| \\ b\cdot\mathrm{C}\cdot a \end{array} \quad \text{and} \quad \begin{array}{c} a\cdot\mathrm{C}\cdot b \\ \| \\ a\cdot\mathrm{C}\cdot b \end{array},$$

"Centrally" or "axially" symmetrical. — "Plane" symmetrical.

he pointed out that, in the conversion of substances of the centrosymmetrical type into saturated compounds, it is a matter of indifference to which of the doubly-bound carbon atoms either part of the additive agent attaches itself, as the products are identical. In the planosymmetrical series, the products of addition are enantiomorphous, but in both cases there are equal chances that *either* of the two common "bonds" may be ruptured, as the molecule is symmetrical

about the plane containing the groups affixed to the doubly-bound pair of carbon atoms. The last condition is also present in the more general case where any doubly-bound carbon atom is attached to two different groups,

$$\begin{array}{c} a\cdot\mathrm{C}\cdot b \\ \| \\ \cdot\mathrm{C}\cdot \end{array},$$

except in the single instance where the molecule is already an asymmetric one, that is to say, where it already contains one or more asymmetric atoms, or is built on one of the types which comply with the conditions necessary for the existence of enantiomorphism, and to which attention was drawn by van 't Hoff in his original treatise. It follows, therefore, that whilst, in general, by the conversion of a group

$$\begin{array}{c} a\cdot\mathrm{C}\cdot b \\ \| \\ \cdot\mathrm{C}\cdot \end{array} \text{ into a saturated one } \begin{array}{c} x \\ \cdot \\ a\cdot\mathrm{C}\cdot b \\ | \\ \cdot\mathrm{C}\cdot \\ \cdot \\ y \end{array}$$

an asymmetric carbon atom is produced, the right- and left-handed individuals are formed in approximately equal numbers,[1] and thus the

[1] In accordance with the usual convention, the enantiomorphous forms here are

$$\begin{array}{c} x \\ \cdot \\ a\cdot\mathrm{C}\cdot b \\ | \\ \cdot\mathrm{C}\cdot \\ \cdot \\ y \end{array} \quad \text{and} \quad \begin{array}{c} x \\ \cdot \\ b\cdot\mathrm{C}\cdot a \\ | \\ \cdot\mathrm{C}\cdot \\ \cdot \\ y \end{array}$$

Throughout the following pages, however, only one of the two mirror images is represented in any instance, as the results here arrived at by the manipulation of the formulæ apply with equal truth to both, and such inactive mixtures will be indicated by the letter (r) affixed to the one formula given. It may be pointed out that a rotation of either carbon atom about the "bond" joining the two may be represented by an exchange in the position of the other three groups attached to that atom providing that their order, clockwise or counter-clockwise, around that carbon atom remains the same; thus, the three figures

$$\begin{array}{c} x \\ \cdot \\ a\cdot\mathrm{C}\cdot b \\ | \\ \cdot\mathrm{C}\cdot \\ \cdot \end{array}, \quad \begin{array}{c} b \\ \cdot \\ x\cdot\mathrm{C}\cdot a \\ | \\ \cdot\mathrm{C}\cdot \\ \cdot \end{array} \quad \text{and} \quad \begin{array}{c} a \\ \cdot \\ b\cdot\mathrm{C}\cdot x \\ | \\ \cdot\mathrm{C}\cdot \\ \cdot \end{array}$$

represent three phases in the rotation of the upper carbon atom about the vertical "bond," as the order *abx* about that atom is counter-clockwise in each case.

For numerous reasons, the parts of the agent added at a double binding will, in all cases, be represented as becoming attached in the mode above indicated, namely, in the line of the original ethylenic linkage, and, inversely, the withdrawal of two groups in the formation of an ethylenic union is imagined to occur only in the

non-production of optically active substances from inactive compounds of this class is at once accounted for.

Malic acid, according to Wislicenus,[1] is probably to be regarded as constituted with opposed carboxyl groups

$$\begin{array}{l} \quad\quad\quad\;\; OH \\ \quad\quad\quad\;\; | \\ CO_2H\cdot C\cdot H \\ \quad\quad\quad\;\; | \\ \quad\;\; H\cdot C\cdot CO_2H \\ \quad\quad\quad\;\; | \\ \quad\quad\quad\;\; H \end{array},$$

the affinity of the carboxyl group for hydrogen doubtless being greater than that of carboxyl for another carboxyl group or for hydroxyl, and the production of fumaric acid,

$$\begin{array}{l} CO_2H\cdot C\cdot H \\ \quad\quad\quad\;\; \| \\ \quad\;\; H\cdot C\cdot CO_2H \end{array},$$

as the main product when the elements of water are withdrawn from malic acid is precisely in agreement with this assumption. The conversion of ethyl maleate into ethyl fumarate by means of iodine was explained by aid of the supposition that di-iodosuccinic acid is the initial product, and the mutual repulsion of the two iodine atoms then results in the rotation of the two parts of the molecule, a more favoured configuration being adopted; from the molecule in this new disposition hydrogen iodide is then withdrawn, a process leading to the production of iodomaleïc acid, which is afterwards converted into maleïc acid itself by the reducing action of the hydrogen iodide present.

$$\begin{array}{l} CO_2H\cdot C\cdot H \\ \quad\quad\quad\;\; \| \\ \quad\;\; H\cdot C\cdot CO_2H \end{array} \longrightarrow \begin{array}{l} \quad\quad\quad\;\; I \\ CO_2H\cdot C\cdot H \\ \quad\quad\quad\;\; | \\ \quad\;\; H\cdot C\cdot CO_2H \\ \quad\quad\quad\;\; I \end{array} (r) \longrightarrow \begin{array}{l} \quad\;\; H \\ I\cdot C\cdot CO_2H \\ \quad\;\; | \\ H\cdot C\cdot CO_2H \\ \quad\;\; I \end{array} (r) \longrightarrow$$

Fumaric acid. Externally compensated di-iodosuccinic acid.

$$\begin{array}{l} I\cdot C\cdot CO_2H \\ \quad\;\; \| \\ H\cdot C\cdot CO_2H \end{array}.$$

Iodomaleic acid.

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instance when they are represented on the paper as in a straight line with the "double bond" about to be formed:

$$\begin{array}{l} \quad x \\ a\cdot C\cdot b \\ \quad | \\ d\cdot C\cdot e \\ \quad y \end{array} \longrightarrow \begin{array}{l} a\cdot C\cdot b \\ \quad \| \\ d\cdot C\cdot c \end{array} + x\cdot y.$$

[1] *Annalen*, 1888, **246**, 53—96.

The process by which hydrobromic acid effects the reverse change of maleïc into fumaric acid was shown to be capable of explanation on similar lines.

In the original memoir presented to the Königl. Sächs. Gesellschaft der Wissenschaften, attention was drawn to certain observations of Petrie and of Bandrowski which appeared to be inconsistent with the theory of the relations of maleïc and fumaric acids therein put forward. Petrie found that fumaric acid is the sole product of the action of bromine on maleïc acid in presence of water at ordinary temperatures, and Bandrowski obtained dibromosuccinic acid as the result of the interaction of bromine and acetylenedicarboxylic acid. Wislicenus was able to show later [1] that these reactions are in reality very complicated, the products being mixtures of a number of compounds such as his theory was capable of explaining.

In replying to certain criticisms of Lossen, Wislicenus took occasion to remark that the conception of atoms as mere material points was antagonistic to his views, for he regarded the atoms as aggregations of the primitive element and analogous to compound radicles, being, therefore, endowed with a space configuration of their own. To his mind it appeared not improbable that the carbon atom has a tetrahedral shape, and that the forces which are displayed in the "affinities" or "bonds" are concentrated in the four corners of this configuration, perhaps for reasons such as lead to the accumulation of the presumably analogous electric charge at the points and corners of a conductor; if so, the carriers of energy must be the primitive atoms, exactly as the chemical energy of compound radicles is the resultant of the energy of the elementary atoms.

Among the first compounds which Wislicenus proceeded to investigate, with the aid of his stereochemical ideas, were the isomeric tolane dichlorides.[2] By the immediate application of van 't Hoff's conception, it was concluded that the product obtained by the direct addition of chlorine to tolane must be the planosymmetric compound $\begin{matrix} C_6H_5\cdot C\cdot Cl \\ \| \\ C_6H_5\cdot C\cdot Cl \end{matrix}$, so that the isomeride of lower melting point is therefore to be represented by the axially symmetrical formula $\begin{matrix} C_6H_5\cdot C\cdot Cl \\ \| \\ Cl\cdot C\cdot C_6H_5 \end{matrix}$.

Wislicenus assigned to β-coumaric acid the structure $\begin{matrix} H\cdot C\cdot C_6H_5\cdot OH \\ \| \\ H\cdot C\cdot CO_2H \end{matrix}$, for the reason that it is more readily converted into the lactone, coumarin, than is the isomeric acid; in order to account for the conversion of the latter into coumarin by hydrogen bromide, the assumption was made that the elements of hydrogen bromide are

[1] *Annalen*, 1888, **246**, 53—96. [2] *Ibid.*, **248**, 1—34.

added at the ethylenic linkage, and that a subsequent internal rotation of the molecule takes place consequent on a supposed inclination towards the formation of the lactone.

The practical investigation of the isomeric crotonic acids fell to his pupils Teisler and Langbein.[1]

The results led him to infer that solid crotonic acid has the structure

$$\begin{array}{l} H\cdot C\cdot CH_3 \\ \;\;\;\, \| \\ H\cdot C\cdot CO_2H \end{array},$$

leaving for the liquid *iso*crotonic acid the formula

$$\begin{array}{r} CH_3\cdot C\cdot H \\ \| \;\;\;\; \\ H\cdot C\cdot CO_2H \end{array}.$$

The former, with chlorine, yielded $\alpha\beta$-dichlorobutyric acid,

$$\begin{array}{l} \;\;\;\;\, Cl \\ H\cdot C\cdot CH_3 \\ \;\;\;\;\, | \\ H\cdot C\cdot CO_2H \\ \;\;\;\;\, Cl \end{array} \;(r)$$

whilst $\alpha\beta$-*iso*dichlorobutyric acid, $\begin{array}{r} Cl \;\;\;\;\;\;\;\; \\ CH_3\cdot C\cdot H \;\;\;\; \\ | \;\;\;\;\;\;\;\; \\ H\cdot C\cdot CO_2H \\ Cl \;\;\;\;\;\;\;\; \end{array}(r)$, was the product from *iso*crotonic acid. By removal of the elements of hydrogen chloride from $\alpha\beta$-*iso*dichlorobutyric acid, the product α-chlorocrotonic acid was obtained,

$$\underbrace{\begin{array}{r} Cl \;\;\;\;\;\;\;\; \\ CH_3\cdot C\cdot H \;\;\;\; \\ | \;\;\;\;\;\;\;\; \\ H\cdot C\cdot CO_2H \\ Cl \;\;\;\;\;\;\;\; \end{array} (r) \longrightarrow \begin{array}{r} Cl \;\;\;\; \\ CH_3\cdot C\cdot H \\ | \;\;\;\; \\ CO_2H\cdot C\cdot Cl \\ H \;\;\;\; \end{array} (r)}_{\alpha\beta\text{-}iso\text{Dichlorobutyric acid.}} \longrightarrow \underset{\alpha\text{-Chlorocrotonic acid.}}{\begin{array}{r} CH_3\cdot C\cdot H \\ \| \;\;\;\; \\ CO_2H\cdot C\cdot Cl \end{array}},$$

and the same substance, when warmed with an aqueous solution of sodium carbonate, by simultaneous loss of carbon dioxide and hydrogen bromide afforded α-*iso*chloropropylene, $\begin{array}{r} CH_3\cdot C\cdot H \\ \| \;\;\;\; \\ H\cdot C\cdot Cl \end{array}$; the latter was rapidly attacked by alkalis at 100°, yielding allylene, $\begin{array}{r} CH_3\cdot C \\ ||| \\ H\cdot C \end{array}$, whilst the isomeric α-chloropropylene, $\begin{array}{r} CH_3\cdot C\cdot H \\ \| \;\;\;\; \\ Cl\cdot C\cdot H \end{array}$, prepared by a similar series of reactions, applied to crotonic acid, reacted with alkalis very much more

[1] *Annalen*, 1888, **248**, 281—355.

slowly, a result which is in harmony with the structures assigned to the isomeric crotonic acids.

The additional observation was made that by heating *αβ*-dichlorobutyric acid a partial conversion of the compound in *αβ-iso*dichlorobutyric acid may be effected.

The study of the relations subsisting between angelic and tiglic acids gave results of an equally interesting character.[1]

Tiglic acid, represented by the formula $\begin{array}{c}H{\cdot}C{\cdot}CH_3\\ \|\\ CH_3{\cdot}C{\cdot}CO_2H\end{array}$, gives a dibromide which, when warmed with sodium carbonate in aqueous solution, is converted into crotonylene hydrobromide,

$$\underset{\text{Tiglic acid.}}{\begin{array}{c}H{\cdot}C{\cdot}CH_3\\ \|\\ CH_3{\cdot}C{\cdot}CO_2H\end{array}} \rightarrow \underbrace{\begin{array}{c}Br\\ H{\cdot}C{\cdot}CH_3\\ |\\ CH_3{\cdot}C{\cdot}CO_2H\\ Br\end{array}(r) \rightarrow \begin{array}{c}Br\\ H{\cdot}C{\cdot}CH_3\\ |\\ Br{\cdot}C{\cdot}CH_3\\ CO_2H\end{array}(r)}_{\text{Tiglic acid dibromide.}} \rightarrow$$

$$\underset{\text{Crotonylene hydrobromide.}}{\begin{array}{c}H{\cdot}C{\cdot}CH_3\\ \|\\ Br{\cdot}C{\cdot}CH_3\end{array}};$$

the isomeric angelic acid yielded in his hands as main product angelic acid dibromide, a compound which had previously been overlooked, and which with sodium carbonate was found to yield *iso*dibromo*pseudo*-butylene,

$$\underset{\text{Angelic acid.}}{\begin{array}{c}CH_3{\cdot}C{\cdot}H\\ \|\\ CH_3{\cdot}C{\cdot}CO_2H\end{array}} \rightarrow \underbrace{\begin{array}{c}Br\\ CH_3{\cdot}C{\cdot}H\\ |\\ CH_3{\cdot}C{\cdot}CO_2H\\ Br\end{array}(r) \rightarrow \begin{array}{c}Br\\ CH_3{\cdot}C{\cdot}H\\ |\\ Br{\cdot}C{\cdot}CH_3\\ CO_2H\end{array}(r)}_{\text{Angelic acid dibromide.}} \rightarrow$$

$$\underset{\textit{iso}\text{Bromo}\textit{pseudo}\text{butylene.}}{\begin{array}{c}CH_3{\cdot}C{\cdot}H\\ \|\\ Br{\cdot}C{\cdot}CH_3\end{array}}.$$

The last-named substance was also obtained by removal of the elements of hydrogen bromide from *pseudo*butylene dibromide,

$$\underset{\textit{pseudo}\text{Butylene.}}{\begin{array}{c}CH_3{\cdot}C{\cdot}H\\ \|\\ CH_3{\cdot}C{\cdot}H\end{array}} \rightarrow \underbrace{\begin{array}{c}Br\\ CH_3{\cdot}C{\cdot}H\\ |\\ CH_3{\cdot}C{\cdot}H\\ Br\end{array}(r) \rightarrow \begin{array}{c}Br\\ CH_3{\cdot}C{\cdot}H\\ |\\ Br{\cdot}C{\cdot}CH_3\\ H\end{array}(r)}_{\textit{pseudo}\text{Butylenedibromide.}} \rightarrow \underset{\textit{iso}\text{Bromo}\textit{pseudo}\text{-butylene.}}{\begin{array}{c}CH_3{\cdot}C{\cdot}H\\ \|\\ Br{\cdot}C{\cdot}CH_3\end{array}}.$$

[1] *Annalen*, 1893, **272**, 1—99; 1893, **274**, 99—119; 1900, **313**, 207—209 210—228

Crotonylene, with bromine, gave $\beta\gamma$-dibromo*pseudo*butylene,

$$\begin{matrix} CH_3{\cdot}C \\ \| \! | \\ CH_3{\cdot}C \end{matrix} \longrightarrow \begin{matrix} CH_3{\cdot}C{\cdot}Br \\ \| \\ CH_3{\cdot}C{\cdot}Br \end{matrix},$$

Crotonylene. $\beta\gamma$-Dibromo*pseudo*butylene.

the isomeride of which, namely, $\beta\gamma$-*iso*dibromo*pseudo*butylene, was prepared by removing the elements of hydrogen bromide from $\beta\gamma\gamma$-tribromobutane,

$$\begin{matrix} CH_3{\cdot}C{\cdot}Br \\ \| \\ CH_3{\cdot}C{\cdot}Br \end{matrix} \longrightarrow \begin{matrix} Br \\ CH_3{\cdot}\dot{C}{\cdot}Br \\ | \\ CH_3{\cdot}C{\cdot}H \\ \dot{Br} \end{matrix} (r) \longrightarrow \begin{matrix} Br \\ CH_3{\cdot}\dot{C}{\cdot}Br \\ | \\ Br{\cdot}C{\cdot}CH_3 \\ \dot{H} \end{matrix} (r)$$

$\beta\gamma$-Dibromo*pseudo*butylene. $\beta\gamma\gamma$-Tribromobutane.

$$\begin{matrix} CH_3{\cdot}C{\cdot}Br \\ \| \\ Br{\cdot}C{\cdot}CH_3 \end{matrix}.$$

iso-$\beta\gamma$-Dibromo*pseudo*butylene.

From both of these dibromo*pseudo*butylenes, the same crotonylene tetrabromide was obtained by addition of bromine.

The hope expressed by Wislicenus in this paper that it might some day be found possible to prepare the hydrobromides of angelic and tiglic acids, and afterwards to convert these into the isomeric *pseudo*butylenes, was, strictly speaking, not realised, although some time later the same end was attained by the employment of the hydriodides of these two acids.[1] Tiglic acid hydriodide, warmed with an aqueous solution of sodium carbonate, lost hydrogen iodide and carbon dioxide, affording a hydrocarbon which, when passed into bromine, gave rise to a dibromide; the latter, on treatment with potassium hydroxide, was converted into *iso*bromo*pseudo*butylene, $\begin{matrix} CH_3{\cdot}C{\cdot}H \\ \| \\ Br{\cdot}C{\cdot}CH_3 \end{matrix}$. Angelic acid, by the same series of reactions, was finally transformed into bromo*pseudo*butylene proper, $\begin{matrix} CH_3{\cdot}C.H \\ \| \\ CH_3{\cdot}C{\cdot}Br \end{matrix}$. These results are exactly in accordance with the general conclusions which Wislicenus had previously drawn, and the changes may be followed in a graphic manner in the case of tiglic acid:—

$$\begin{matrix} CH_3C{\cdot}H \\ \| \\ CO_2H{\cdot}C{\cdot}CH_3 \end{matrix} \longrightarrow \begin{matrix} I \\ CH_3{\cdot}\dot{C}{\cdot}H \\ | \\ CO_2H{\cdot}C{\cdot}CH_3 \\ \dot{H} \end{matrix} (r) \longrightarrow \begin{matrix} I \\ CH_3{\cdot}\dot{C}{\cdot}H \\ | \\ CH_3{\cdot}C{\cdot}H \\ \dot{C}O_2H \end{matrix} (r) \longrightarrow$$

Tiglic acid. Tiglic acid hydriodide.

[1] Wislicenus, Talbot, and Henze, *Annalen*, 1900, **313**, 228—242.

$$\begin{array}{c} CH_3\cdot C\cdot H \\ \| \\ CH_3\cdot C\cdot H \end{array} \longrightarrow \begin{array}{c} Br \\ | \\ CH_3\cdot C\cdot H \\ | \\ CH_3\cdot C\cdot H \\ | \\ Br \end{array} \longrightarrow \begin{array}{c} CH_3 \\ | \\ H\cdot C\cdot Br \\ | \\ CH_3\cdot C\cdot H \\ | \\ Br \end{array} \longrightarrow \begin{array}{c} CH_3\cdot C\cdot H \\ \| \\ Br\cdot C\cdot CH_3 \end{array}\cdot$$

*pseudo*Butylene.	*pseudo*Butylene dibromide (meso).	*iso*Bromo*pseudo*-butylene.

Fittig and Pagenstecher had actually observed that angelic acid when brominated yielded tiglic acid dibromide as main product; the difference between these results and those of Wislicenus and Pückert proved to be due to the fact that unless a low temperature be maintained during the addition of bromine, and strong light carefully excluded, isomeric change of the angelic to tiglic dibromide may occur. Wislicenus was not disposed to assume an undue amount of credit for his discovery of the true dibromide of angelic acid which Fittig and Pagenstecher had overlooked, but drew attention to the circumstance that the draught cupboards in Fittig's laboratory at Strassburg were placed in the windows, and thus received a strong light, whilst in his own laboratory at Leipzig they lay between the windows, otherwise, as he remarked, angelic acid dibromide might have remained unknown.[1]

Later, with Schmidt, Wislicenus prepared *pseudo*butylene by the method employed by Le Bel and Greene, namely, by the dehydration of *iso*butyl alcohol. It was found[2] that a mixture of the centrosymmetrical and planosymmetrical hydrocarbons was formed, and the mixture of dibromides made by passing the mixture of hydrocarbons into bromine was separated into two portions by fractional distillation. The higher boiling portion, on treatment with potassium hydroxide, yielded the bromo-derivative of the planosymmetrical *pseudo*butylene, $\begin{array}{c} CH_3\cdot C\cdot H \\ \| \\ CH_3\cdot C\cdot Br \end{array}$, in larger quantity than did the lower boiling fraction, but the main product from both was the bromo-derivative of the centrosymmetrical hydrocarbon, $\begin{array}{c} CH_3\cdot C\cdot H \\ \| \\ Br\cdot C\cdot CH_3 \end{array}$, which in presence of hydrogen bromide or on exposure to sunlight was found to undergo a slow conversion into its stereoisomeride. Of the two bromo*pseudo*-butylenes, the one assigned the formula $\begin{array}{c} CH_3\cdot C\cdot H \\ \| \\ CH_3\cdot C\cdot Br \end{array}$ gave crotonylene the more readily when heated with potassium hydroxide, an observation quite in accordance with the relative position of the hydrogen and bromine atoms in the formulæ assigned.

Henze assisted in adducing new evidence in support of Wislicenus's

[1] *Annalen*, 1893, **272**, 98. [2] *Ibid.*, 1900, **313**, 210—228.

view.[1] The dibromide of angelic acid, as was anticipated, yielded β-bromotiglic acid under the influence of strong potassium hydroxide, whilst the dibromide of tiglic acid was converted into β-bromoangelic acid,

$$\begin{matrix} CH_3\cdot C\cdot H \\ CH_3\cdot C\cdot CO_2H \end{matrix} \longrightarrow \begin{matrix} Br \\ CH_3\cdot C\cdot H \\ CH_3\cdot C\cdot CO_2H \\ Br \end{matrix} (r) \longrightarrow \begin{matrix} H \\ Br\cdot C\cdot CH_3 \\ CH_3\cdot C\cdot CO_2H \\ Br \end{matrix} (r) \longrightarrow$$

Angelic acid. Angelic acid dibromide.

$$\longrightarrow \begin{matrix} Br\cdot C\cdot CH_3 \\ CH_3\cdot C\cdot CO_2H \end{matrix} .$$

β-Bromotiglic acid.

$$\begin{matrix} H\cdot C\cdot CH_3 \\ CH_3\cdot C\cdot CO_2H \end{matrix} \longrightarrow \begin{matrix} Br \\ H\cdot C\cdot CH_3 \\ CH_3\cdot C\cdot CO_2H \\ Br \end{matrix} (r) \longrightarrow \begin{matrix} H \\ CH_3\cdot C\cdot Br \\ CH_3\cdot C\cdot CO_2H \\ Br \end{matrix} (r) \longrightarrow$$

Tiglic acid. Tiglic acid dibromide.

$$\longrightarrow \begin{matrix} CH_3\cdot C\cdot Br \\ CH_3\cdot C\cdot CO_2H \end{matrix} .$$

β-Bromoangelic acid.

Of these β-bromo-unsaturated acids, the latter was the more easily converted into crotonylene by means of sodium carbonate solution, an observation which again is in harmony with the conclusions previously formed, as this isomeride is the one to which was assigned the formula having the bromine atom and the carboxyl group in the position most favourable to the occurrence of this change.

Stilbene gave Wislicenus and Seeler two dibromides, the main product being the α-derivative, which was considered to be the normal product, although, unlike the great majority of such normal addition products, it was found to be produced in larger proportion at a high temperature and in presence of intense light.[2] Either dibromide, when heated, underwent a partial conversion into the other; both yielded monobromostilbenes on treatment with alkalis, the α-compound affording an oily bromostilbene, the latter a crystalline one, and of these the crystalline compound was the more easily converted into tolane when boiled with alcoholic potassium hydroxide, showing that it has the structure $\begin{matrix} C_6H_5\cdot C\cdot H \\ C_6H_5\cdot C\cdot Br \end{matrix}$. These observations led to the following view of the changes studied :—

[1] *Annalen*, 1900, **313**, 243—250. [2] *Ber.*, 1895, **28**, 2693—2703.

$$\begin{array}{c} C_6H_5\cdot C\cdot H \\ \| \\ C_6H_5\cdot C\cdot H \end{array} \rightarrow \begin{array}{c} Br \\ C_6H_5\cdot C\cdot H \\ C_6H_5\cdot C\cdot H \\ Br \end{array} \rightarrow \begin{array}{c} Br \\ C_6H_5\cdot C\cdot H \\ Br\cdot C\cdot C_6H_5 \\ H \end{array} \rightarrow \begin{array}{c} C_6H_5\cdot C\cdot H \\ \| \\ Br\cdot C\cdot C_6H_5 \end{array}$$

Stilbene. α-Stilbene dibromide (internally compensated). Oily dibromo-stilbene.

$$\downarrow \quad \begin{array}{c} C_6H_5\cdot C \\ ||| \\ C_6H_5\cdot C \end{array}$$

Tolane.

$$\begin{array}{c} C_6H_5\cdot C\cdot H \\ \| \\ H\cdot C\cdot C_6H_5 \end{array} \rightarrow \begin{array}{c} Br \\ C_6H_5\cdot C\cdot H \\ H\cdot C\cdot C_6H_5 \\ Br \end{array} (r) \rightarrow \begin{array}{c} Br \\ C_6H_5\cdot C\cdot H \\ C_6H_5\cdot C\cdot Br \\ H \end{array} (r) \rightarrow \begin{array}{c} C_6H_5\cdot C\cdot H \\ \| \\ C_6H_5\cdot C\cdot Br \end{array}$$

*iso*Stilbene (?) β-Stilbene dibromide (externally compensated). Crystalline bromostilbene.

Although at the time no direct evidence as to the existence of isomeric stilbenes could be adduced, Wislicenus with Jahrmarkt afterwards succeeded in obtaining centrosymmetrical *iso*stilbene[1] by reducing the oily bromostilbene from α-stilbenedibromide.

$$\begin{array}{c} C_6H_5\cdot C\cdot H \\ \| \\ Br\cdot C\cdot C_6H_5 \end{array} \longrightarrow \begin{array}{c} C_6H_5\cdot C\cdot H \\ \| \\ H\cdot C\cdot C_6H_5 \end{array}.$$

Oily bromostilbene. *iso*Stilbene.

This hydrocarbon, unlike stilbene itself, is a liquid which yields ordinary stilbene when distilled under atmospheric pressure, or when left with traces of bromine or iodine ; when dissolved in carbon disulphide and mixed with bromine in absence of light it gives β-stilbene dibromide to the extent of 83 per cent. of that theoretically possible.

The investigation of stereoisomerism in cyclic compounds led Wislicenus, with Peters, Schramm and Mohr, to a study of the isomeric forms of ββ'-dibromohexane.[2] On heating this dibromo-compound with ethyl disodiomalonate, an oil having the composition of a diethyl dimethyl*cyclo*pentanedicarboxylate was formed, and this, on hydrolysis, afforded a mixture of ester-acids, dicarboxylic acids, and monocarboxylic acids, each of which was shown to be related to one or other of the two dimethyl*cyclo*pentanedicarboxylic acids,

$$\begin{array}{c} CH_2 \\ | \\ H\cdot C\cdot CH_3 \\ | \\ CO_2H\cdot C\cdot CO_2H \\ | \\ H\cdot C\cdot CH_3 \\ | \\ CH_2 \end{array} (m) \quad \text{and} \quad \begin{array}{c} CH_2 \\ | \\ H\cdot C\cdot CH_3 \\ | \\ CO_2H\cdot C\cdot CO_2H \\ | \\ CH_3\cdot C\cdot H \\ | \\ CH_2 \end{array} (r).$$

cis-cis. *cis-trans.*

[1] *Ber. K. Sächs. Wiss. Math. Phys. Ch.*, 1900, **52**, 117—123.
[2] *Ber.*, 1901, **34**, 2565—2583.

The constitution of the two acids was ascertained by heating them so as to cause the loss of one molecular proportion of carbon dioxide, and in these circumstances one of them gave rise to two stereoisomeric monocarboxylic acids, and the other to one monocarboxylic acid only. The former must have been produced from the *cis-cis* derivative and the latter from the *cis-trans*-one.

The formulæ of the isomerides from the *cis-cis*-dicarboxylic acid are

$$\begin{array}{r} CH_2\text{—} \\ H\cdot C\cdot CH_3 \\ H\cdot C\cdot CO_2H \\ H\cdot C.CH_3 \\ CH_2\text{—} \end{array} (m) \quad \text{and} \quad \begin{array}{r} CH_2\text{—} \\ H\cdot C\cdot CH_3 \\ CO_2H\cdot C\cdot H \\ H\cdot C\cdot CH_3 \\ CH_2\text{—} \end{array} (m),$$

and represent internally compensated inactive compounds. Those of the possible products arising from the *cis-trans*-dicarboxylic acid, in the same manner, are

$$\begin{array}{r} CH_2\text{—} \\ H\cdot C\cdot CH_3 \\ H\cdot C\cdot CO_2H \\ CH_3\cdot C\cdot H \\ CH_2\text{—} \end{array} (r) \quad \text{and} \quad \begin{array}{r} CH_2\text{—} \\ H\cdot C\cdot CH_3 \\ CO_2H\cdot C\cdot H \\ CH_3\cdot C\cdot H \\ CH_2\text{—} \end{array} (r),$$

but these are in reality identical, and represent one of the two enantiomorphous forms of an inactive mixture.

The $\beta\beta'$-dibromohexane employed was separated by freezing into two parts, one solid and the other a liquid; the former of these, when condensed with ethyl disodiomalonate, afforded ethyl *cis cis*-dimethyl*cyclo*pentanedicarboxylate, and was, therefore, the meso-compound

$$\begin{array}{c} CH_3 \\ H\cdot C\cdot Br \\ CH_2 \\ CH_2 \\ H\cdot C\cdot Br \\ CH_3 \end{array}$$

the liquid isomeride, on the other hand, gave rise to the *cis-trans*-dicarboxylic derivative, and was, therefore, an inactive mixture of the *d*- and *l*-compounds.

It is perhaps hardly necessary to say that the foregoing sketch deals only with a part of the scientific work which was carried out by Wislicenus himself or by his pupils under his direction. No mention has been made of his recent contributions to the study of

the reactions of dichloroether,[1] his investigations on the interaction of chloral with ketones,[2] on adipinketone,[3] of his discovery of the true vinylacetic acid,[4] or of his numerous researches on the stereoisomerism of the cyclic pinacones obtained by the reduction of diketones.[5] To each of these much interest attaches, but considerations of space have led me to select from his more recent work that part which appears to have the most importance in connection with the growth of the science of stereochemistry, with which his name is indissolubly connected.

During the last few years of his life, Wislicenus became more and more the victim of severe attacks of ill-health, against which he fought with all his fine energy and determination, working steadily almost to the last. In the summer of 1902, he found his most strenuous efforts at resistance unavailing, and at last took refuge in complete rest at health resorts. His condition in the autumn gave his friends cause for the gravest anxiety, and early in the morning of December 5th, 1902, he passed away.

Two days later, a mournful but impressive ceremony was seen in the lecture-room attached to the Leipzig Chemical Laboratory; Beckmann, Ostwald, His, Lüty, Hantzsch, Medicus, and Bucher, colleagues of Wislicenus, representing their respective departments and faculties, expressed in moving terms their appreciation of the exalted and many-sided character of their departed friend.

The concluding words which fell from Ostwald were these:—"Und wenn wir betrachtend vor ihnen stehen, so fühlen wir es lebendig; du warst nicht nur ein grosser Forscher, du warst auch ein guter Mensch!" and this is the note which persistently rings in the memory of all who have tried to understand the man.

There can be no doubt that in Wislicenus the world lost a man, not only of great and many-sided ability, but also of extraordinary directness of purpose and splendid character.

[1] *Annalen*, 1884, **226**, 261—281; 1888, **243**, 151—192.
[2] *Ber.*, 1893, **26**, 908—915.
[3] *Annalen*, 1893, **275**, 312—382.
[4] *Ber.*, 1899, **32**, 2047—2048.
[5] *Annalen*, 1898, **302**, 191—244.

ANNUAL GENERAL MEETING,

March 29th, 1905.

Professor W. A. Tilden, D.Sc., F.R.S., in the Chair.

The President declared the ballot open for the election of Officers and Council for the ensuing year, Dr. A. E. H. Tutton and Mr. A. G. Bloxam being appointed Scrutators. He then presented the following Report on the state of the Society during the past twelve months:

Report of the Council.

The Council are glad to be in the position to report that the Society continues to flourish, and that, as measured by the number of papers read, its activity has exceeded that of any previous year.

On December 31st, 1903, the number of Fellows was 2,700. During 1904, 128 Fellows were elected, and 5 reinstated, making a gross total of 2,833. The Society has lost 28 Fellows by death; 37 have resigned; the elections of 4 have become void; 52 have been removed for non-payment of subscriptions, and 1 Fellow has withdrawn. The total number of Fellows, therefore, on December 31st, 1904, was 2,711.

The names of the Fellows who have died are:

A. H. Allen.
F. E. Allhusen.
J. Barclay.
Sir I. L. Bell.
F. B. Benger.
C. Beringer.
H. N. Bilimoria.
W. Chattaway.
P. L. Dey.
T. H. Dodd.
W. H. Dodd.
R. E. Doran.
W. Francis.
A. Gibson.
C. G. Grenfell.
H. Grimshaw.
G. Howsam.
T. Isherwood.
J. Jackson.
A. Kitchin.
J. Mason.
D. Munro.
T. A. Pooley.
H. St. John.
C. J. Sawer.
W. H. Stanger.
R. M. W. Swan.
A. W. Williamson.

The following Fellows have resigned :

G. Ansdell.	J. Edmunds.	C. S. Purcell.
J. F. Ballard.	T. A. Ellwood.	A. Sandford.
J. Bardsley.	F. A. Gatty.	W. Sessions.
H. H. Barker.	H. Gordon.	M. J. Sheridan.
G. E. Battle.	G. M. Gregory.	W. Taverner.
J. Baynes.	H. E. Haddon.	G. Trench.
J. Bottomley.	W. Hampton.	H. F. Waller.
G. W. Burman.	E. C. Ibbotson.	A. W. Warrington.
W. F. Butcher.	A. W. D. Leahy.	A. L. White.
J. Caley.	A. E. McKenzie.	H. F. A. Wigley.
H. M. Chapman.	T. R. Marshall.	B. Winstone.
T. A. Dickson.	W. Marshall.	
E. Dowzard.	C. A. Mitchell.	

Among the Fellows removed by death, the Society mourns the loss of Prof. Alexander W. Williamson, who twice filled the office of President, and to whose initiative the publication of the *Abstracts* was largely due.

The number of Honorary and Foreign Members at the date of the last Annual General Meeting was 30. Six names were added to the list by the election on May 18th, 1904, of Prof. A. H. Becquerel, Prof. C. A. Lobry de Bruyn, Prof. F. W. Clarke, Madame M. Curie, Prof. C. Liebermann, and Prof. E. W. Morley. The Society has to lament the death of one of the newly elected Members, Prof. C. A. Lobry de Bruyn, on July 23rd, 1904. The number of Honorary and Foreign Members, therefore, is 35.

During the year 1904, 215 scientific communications have been made to the Society, 188 of which have already been published in the *Transactions*, and abstracts of all have appeared in the *Proceedings*.

The volume of *Transactions* for 1904 contains 175 memoirs, occupying 1,761 pages, whilst that for the preceding year contains 142 memoirs, which occupy 1,490 pages.

The *Journal* for 1904 contains also 4,617 abstracts of papers published mainly in foreign journals, which extend to 1,920 pages, whilst the abstracts for 1903 numbered 3,882 and occupied 1,640 pages.

The abstracts for 1904 may be classified as follows :

Part I.

		Pages.	No. of Abstracts.
Organic Chemistry		1,072	1,968

Part II.

General and Physical Chemistry		606
Inorganic Chemistry		541
Mineralogical Chemistry		132
Physiological Chemistry		501
Chemistry of Vegetable Physiology and Agriculture		311
Analytical Chemistry		558
	848	2,649
Total in Parts I. and II.	1,920	4,617

Owing to the great increase in the number of papers abstracted, it has become necessary to add to the editorial staff. Dr. C. H. Desch has been appointed Assistant Sub-editor, with the object of taking part in the preparation of abstracts for the press, and of relieving Mr. Greenaway of a portion of the clerical work.

Although an award of the Faraday Medal was made in 1895, fifteen years have elapsed since the delivery of the last Faraday Lecture. On April 19th, 1904, the Lecture was delivered by Professor Ostwald, in the lecture theatre of the Royal Institution, the use of which had been kindly granted by the Managers for the occasion. The subject of the Lecture was "Elements and Compounds."

The Wislicenus Memorial Lecture was delivered by Prof. W. H. Perkin on January 25th of the present year.

On the occasion of the celebration of the Jubilee of the Doctorate of Sir Henry E. Roscoe, a Past President of the Society, on April 22nd, 1904, the Council welcomed the opportunity of sending an address of congratulation to him.

Proposals have been received from the Chemical, Metallurgical, and Mining Society of South Africa, and from the American Chemical Society, for a reciprocal exchange of Journals for members of each of these Societies and of the Chemical Society at a rate just sufficient to cover the cost of printing, addressing, and postage. After careful consideration, the Council were unable to accede to the proposals, as the effect on the finances of the Society could not be estimated, and a

limit could not be set to the number of Societies which might seek the benefit of a similar exchange of Journals.

The question of co-operation in the preparation of Abstracts in English has been raised afresh by the American Chemical Society by the appointment of a committee to confer with the Chemical Society on this important subject. The Council have reappointed the Committee which discussed the possibility of co-operation in 1899, and await the proposals of the American Committee with every desire to consider their practicability.

Acting on the suggestion made in the Presidential address at the last Annual General Meeting, the Council have arranged for the preparation and publication of a series of Reports on the advance made each year in chemistry. These reports will be issued early in each year, and it is hoped that they will prove to be of value not only to the Fellows, but to students of chemistry generally.

Obituary notices of several deceased Past Presidents have not as yet been published. These notices have now been received and are in type. Among them is included an obituary notice of Sir Edward Frankland, as the Council have been unable to obtain the manuscript of the Memorial Lecture, delivered on October 31st, 1901.

A further increase in the use of the Library has to be recorded, 1,057 books being borrowed during 1904, as against 991 during the previous year. The additions to the Library comprise 119 books, of which 67 were presented, 296 volumes of periodicals, and 52 pamphlets, as against 126 books, 271 volumes of periodicals, and 43 pamphlets last year. An alteration in the wording of Library Rule IV. has been made to enable new books to be borrowed at an earlier date than formerly.

The Society has been the fortunate recipient of the eudiometer used by the late Sir Edward Frankland in the analysis of ethyl in 1849, presented by Professor Frankland; of a bronze medal of Roger Bacon, presented by Mr. Oscar Guttmann; and of an engraving of Berzelius, presented by Professor Retzius, of Stockholm.

A special Committee was appointed last June to revise the Byelaws, and reported in due course to the Council. The revised Byelaws were submitted by the Council to the Society for consideration at an Extraordinary General Meeting on February 8th, but failed to secure acceptance, being referred back for further consideration.

A memorial, bearing the signatures of nineteen women engaged in chemical work, praying for the admission of women to the Fellowship of the Society, has been under consideration. The Council were advised that "married women are not eligible for election as Fellows of the Society; that it is extremely doubtful

whether the Charter admits of the election of unmarried women as Fellows; that it would not be wise to elect even unmarried women without first applying for a supplemental Charter; and that the election of women as Associates would be legal after a modification of the Bye-laws expressly authorising their election." An alteration in Bye-law III. extending the privileges of the Associateship to women accordingly formed one of the changes in the Bye-laws recently proposed by the Council.

The third Report of the Joint International Committee on Atomic Weights, with its revised table of atomic weights, has been issued to the Fellows in the *Proceedings*.

Grants amounting in all to £215 have been made during the year from the Research Fund, and £26 16*s*. 6*d*. has been returned. Of the papers published in the *Transactions* during 1904, thirty-two were contributed by authors to whom grants had been made from the Research Fund.

The total income of the Society for the year 1904 was £6,700 5*s*. 8*d*. and the expenditure £5,982 14*s*. 6*d*.; in 1903, these were £6,817 19*s*. 7*d*. and £5,926 18*s*. 3*d*. respectively, so that whilst the income has fallen by £117 13*s*. 11*d*., the expenditure has risen by £55 16*s*. 3*d*. A glance at the balance sheet for 1903, however, shows receipts amounting to £257 which cannot be regarded truly as income from normal sources; in 1904 only £5 was so received. Allowing for these items, the income for 1904 shows an increase over that of 1903 of £134 6*s*. 1*d*.

The Treasurer's chief anxiety is due to the ever-increasing size of the *Journal* and the corresponding increase in cost. Both exceed those of 1903, the size by about 17 per cent. and the cost by about 10 per cent., the excess due to printing alone in 1904 amounting to £280 12*s*. 1*d*., whilst the total increase in cost reaches the large sum of £365 6*s*. 11*d*. Part of this is due to the fact that the January number for 1904 contained a double set of Abstracts, thus leading to an increase both in Abstractors' fees and in printing, these two items really representing thirteen months instead of twelve. As pointed out by the President on resigning the Treasurership two years ago, the steady increase in the size and cost of the *Journal* seems to render it inevitable "that, in the "near future, some more stringent regulations both as to the state of "the manuscript and the dimensions of the papers will have to be "imposed" if the Society is to carry on its work of publication efficiently. In addition to the cost of the *Journal*, there is in the present accounts a sum of £237 6*s*. 0*d*. for the printing of Vol. IV, Part 1 (Authors) of the Collective Index (1893—1902). On the other hand, there has been a saving of £42 14*s*. 5*d*. in the cost of the *Proceedings*. The Library

has cost less by the sum of £150 13*s.* 3*d.*, and the general administrative expenses, which in 1903 were abnormally high, owing to special circumstances, have fallen from £1,138 5*s.* 5*d.* to £893 1*s.* 0*d.*, a saving of £245 4*s.* 5*d.*, notwithstanding the cost of introducing house telephones and also connecting the Society with the Post Office system.

The Treasurer reports that the new system of keeping the Society's accounts has been in full working order for two years and has been found most satisfactory in every way.

The Council desire to place on record their appreciation of the valuable services rendered to the Society by Professor Wynne, and an expression of their regret that his removal from London obliges him to relinquish the office of Senior Secretary. By placing him among the Vice-Presidents, it is hoped that the Society may continue to receive the advantage of his experienced co-operation in the work of the Council.

The Treasurer made a statement as to the Society's income and expenditure during the past Session, and proposed a vote of thanks to the Auditors, which was seconded by Dr. L. T. Thorne, carried unanimously, and acknowledged by Mr. E. Grant Hooper.

BALANCE SHEET.—THE CHEMICAL SOCIETY, 31ST DECEMBER, 1904.

Liabilities.

	£ s. d.	£ s. d.
To Subscriptions received in advance		257 0 0
,, Sundry Creditors		895 9 6
,, Research Fund :—		
As per last Balance Sheet	6742 10 1	
Add Excess of Income over Expenditure for the year	42 7 7	
		6784 17 8
,, Chemical Society :—		
As per last Balance Sheet...	17981 10 4	
Add Excess of Income over Expenditure for the year	717 11 2	
		18699 1 6
(The liability in respect of Life Compositions is not included.)		
		£26636 8 8

Assets.

	£ s. d.	£ s. d.
By Investments (value when acquired):—		
£1050 London and North Western Railway 3 per cent. Debenture Stock	839 12 0	
£6730 Metropolitan Consolidated 3½ per cent. Stock	7212 8 6	
£1520 14*s*. 3*d*. Cardiff Corporation 3 per cent. Stock	1650 0 0	
£1400 India 2½ per cent. Stock	1316 1 0	
£2400 Bristol Corporation 2½ per cent. Debenture Stock	2070 2 0	
£2358 Midland Railway 2½ per cent. Preference Stock	2072 8 0	
£1200 Leeds Corporation 3 per cent. Stock	1143 1 0	
£1500 Transvaal 3 per cent. Guaranteed Stock ...	1460 13 6	
		17764 6 0
(Estimated present value of Investments, £16,743 12*s*. 4*d*.)		
,, Library Furniture, Stock of Publications, &c. (not valued)		
,, Sundry Debtors :—		
Society of Public Analysts	11 0 6	
Advertising Agents	57 16 1	
Messrs. Gurney & Jackson	373 9 2	
Telephone Deposit	1 0 0	
		443 5 9
,, Subscriptions in Arrear. Estimated to realise		330 0 0
,, Insurance paid in advance		37 14 3
,, Cash :—		
Deposit Account...	1300 0 0	
Less Overdraft on Current Account	41 11 9	
	1258 8 3	
In hand	17 16 9	
		1276 5 0
,, Research Fund :—		
Investments (value when acquired):		
£1000 North British 4 per cent. No. 1 Preference Stock	1010 0 0	
£4400 Metropolitan Consolidated 3½ per cent. Stock	4587 18 0	
£1034 Great Western Railway 2½ per cent. Debenture Stock	1049 15 11	
	6647 13 11	
,, Cash at Bank	137 3 9	
		6784 17 8
(Estimated present value of Research Fund Investments, £6670 17*s*. 2*d*.)		
		£26636 8 8

INCOME AND EXPENDITURE ACCOUNT

Income.

		£	s.	d.	£	s.	d.
To Life Compositions ...		370	0	0			
,, Admission Fees ...		556	0	0			
,, Annual Subscriptions ...		4307	0	0			
,, Cash on account of Subscriptions and Fees of past years, per Mr. R. Steele ...		5	0	0			
					5238	0	0
,, Investments :—							
Dividends on £6,730 Metropolitan Consolidated 3½ per cent. Stock ...		224	5	6			
£1,050 London and North Western Railway 3 per cent. Debenture Stock ...		30	0	6			
£1,520 14*s*. 3*d*. Cardiff Corporation 3 per cent. Stock ...		43	8	7			
£1,400 India 2½ per cent. Stock ...		33	6	6			
£2,358 Midland Railway 2½ per cent. Preference Stock		56	3	10			
£2,400 Bristol Corporation 2½ per cent. Debenture Stock		57	0	0			
£1,200 Leeds Corporation 3 per cent. Stock ...		34	5	6			
£1,500 Transvaal 3 per cent. Guaranteed Stock ...		42	15	0			
Income Tax Recovered (two years) ...		48	2	8			
Interest on Deposit Account ...		20	0	9			
					589	8	10
,, Publications:—							
Sales :							
Journals ...		748	8	9			
Proceedings ...		15	18	6			
General Index ...		79	15	6			
Memorial Lectures ...		14	13	4			
Library Catalogue ...		3	16	6			
Atomic Weight Tables ...		1	2	7			
Jubilee Volume ...		0	6	0			
		864	1	2			
Less Publishers' Commission ...		84	5	8			
		779	15	6			
Proceeds of Advertisements in Journal...	£85 8 3						
Less Commission ...	12 16 5						
		72	11	10			
					852	7	4
,, Subscriptions from other Societies :—							
Society of Chemical Industry ...		9	9	0			
Society of Public Analysts ...		11	0	6			
					20	9	6
					£6700	5	8

I have examined the above Accounts with the Books and Vouchers of the Society, and and the Investments.

9th March, 1905.

W. B. KEEN,
Chartered Accountant.

FOR THE YEAR ENDED 31ST DECEMBER, 1904.

Expenditure.

	£	s.	d.	£	s.	d.
By Expenses on account of Journal and Proceedings :—						
Salary of Editor ...	300	0	0			
Salary of Sub-Editor ...	200	0	0			
Salary of Indexer ...	80	0	0			
Editorial Postages, &c. ...	19	10	1			
Abstractors' Fees ...	482	10	2			
Printing of Journal ...	2203	7	11			
Printing of Advertisements ...	29	3	0			
Printing of Wrappers ...	112	15	0			
Distribution of Journal ...	425	3	11			
Authors' Copies ...	109	19	6			
				3962	9	7
Printing of Proceedings ...	183	9	5			
Distribution of Proceedings ...	32	4	9			
				215	14	2
,, Purchase of Back Numbers of Journal ...				15	4	5
,, List of Fellows ...				67	4	6
,, Collective Index :—						
Printing Vol. IV., Part I. ...	237	6	0			
Salaries ...	133	15	8			
				371	1	8
,, Library Expenses :—						
Salary of Librarian ...	100	0	0			
Books and Periodicals ...	242	5	10			
Binding ...	53	18	4			
				396	4	2
,, Indexing for International Catalogue ...				30	0	0
,, Faraday Lecture, Honorarium ...	25	0	0			
,, Faraday Lecture, Expenses ...	4	2	6			
				29	2	6
,, Illuminated Address to Sir H. E. Roscoe ...				2	12	6
,, Administrative Expenses :—						
Tea Expenses ...	26	13	5			
Salary of Assistant Secretary...	150	0	0			
Salary of Office and Library Assistant ...	40	6	0			
Wages (Commissionaire, Housekeeper, and Charwoman) ...	137	6	3			
Pension, Mrs. Hall ...	30	0	0			
Coal and Lighting ...	42	13	7			
House Expenses and Repairs ...	77	2	9			
House Telephones ...	32	10	0			
Insurance ...	6	17	2			
Accountants' Charges ...	10	10	0			
Accountants' Commission on Recovery of Income Tax ...	3	9	4			
Legal Charges ...	16	1	6			
Miscellaneous Printing ...	81	7	6			
Stationery ...	45	15	1			
Furniture ...	39	3	6			
Postages...	106	17	7			
Indexing Council Minutes ...	15	15	0			
Miscellaneous Expenses ...	30	12	4			
				893	1	0
,, Balance, being Excess of Income over Expenditure, carried to Balance Sheet ...				717	11	2
				£6700	5	8

certify them to be in accordance therewith. I have also verified the Balance at the Bankers

Approved— John Wade, E. Grant Hooper, Hy. Forster Morley, } *Auditors.*

Research Fund Income and Expenditure Account for the Year ended 31st December, 1904.

Income.

	£ s. d.	£ s. d.
To Dividends:—		
On £4400 Metropolitan Consolidated 3½ per cent. Stock	146 12 6	
On £1000 North British Railway 4 per cent. No. 1 Preference Stock	38 2 3	
On £1034 Great Western Railway 2½ per cent. Debenture Stock	24 12 9	
		209 7 6
,, Repayment of Research Grants:—		
H. E. W. Phillips	20 14 1	
F. E. Matthews	1 2 5	
H. A. Auden	5 0 0	
		26 16 6
,, Repayment of Income Tax (2 years)		21 3 7
		£257 7 7

Expenditure.

	£ s. d.	£ s. d.
By Grants to—		
J. B. Cohen	15 0 0	
A. W. Crossley	10 0 0	
F. E. Francis	10 0 0	
A. Lapworth	15 0 0	
H. R. Le Sueur	10 0 0	
T. M. Lowry	10 0 0	
R. S. Morrell	10 0 0	
R. H. Pickard	10 0 0	
C. Smith	5 0 0	
J. J. Sudborough	20 0 0	
G. Tattersall	10 0 0	
J F. Thorpe	10 0 0	
R. D. Abell	5 0 0	
H. D. Dakin	10 0 0	
A. McKenzie	25 0 0	
J. W. Mellor	10 0 0	
H. A. Miers	20 0 0	
W. E. S. Turner	5 0 0	
F. G. Pope	5 0 0	
		215 0 0
,, Balance, being excess of Income over Expenditure, carried to Balance Sheet		42 7 7
		£257 7 7

I have examined the above Account with the Books and Vouchers of the Society, and certify it to be in accordance therewith. I have also verified the Balance at the Bankers and the Investments.

9th March, 1905.

W. B. Keen,
Chartered Accountant.

Approved— John Wade, E. Grant Hooper, Hy. Forster Morley, *Auditors.*

Mr. W. J. Sell moved the adoption of the Report; this was seconded, and carried unanimously.

The President then delivered his address, which will be found on page 546.

Professor Raphael Meldola proposed a vote of thanks to the President, coupled with the request that he would allow the Address to be printed in the *Transactions*. Professor G. Carey Foster seconded the motion, which was carried by acclamation, and acknowledged by the President.

Professor H. McLeod proposed a vote of thanks to the Treasurer, Secretaries, Foreign Secretary, and Council for their services during the past year. This was seconded by Dr. J. A. Voelcker, and unanimously adopted. Professor W. P. Wynne responded.

The Scrutators then presented their Report to the President, who declared the following to have been duly elected as Officers and Council for the ensuing year.

President: Raphael Meldola, F.R.S.

Vice-Presidents who have filled the office of President: H. E. Armstrong, Ph.D., LL.D., F.R.S.; A. Crum Brown, D.Sc., LL.D., F.R.S.; Sir William Crookes, D.Sc., F.R.S.; Sir James Dewar, M.A., LL.D., F.R.S.; A. Vernon Harcourt, M.A., D.C.L., F.R.S.; H. Müller, Ph.D., LL.D., F.R.S.; W. Odling, M.A., M.B., F.R.S.; W. H. Perkin, Ph.D., LL.D., F.R.S.; J. Emerson Reynolds, Sc.D., M.D., F.R.S.; Sir Henry E. Roscoe, LL.D., F.R.S.; W. J. Russell, Ph.D., F.R.S.; T. E. Thorpe, C.B., LL.D., F.R.S.; W. A. Tilden, D.Sc., F.R.S.

Vice-Presidents: Horace T. Brown, LL.D., F.R.S.; Harold B. Dixon, M.A., F.R.S.; Wyndham R. Dunstan, M.A., LL.D., F.R.S.; David Howard; A. Smithells, B.Sc., F.R.S.; W. P. Wynne, D.Sc., F.R.S.

Secretaries: M. O. Forster, D.Sc., Ph.D.; A. W. Crossley, D.Sc., Ph.D.

Foreign Secretary: Sir W. Ramsay, K.C.B., LL.D., F.R.S.

Treasurer: Alexander Scott, M.A., D.Sc., F.R.S.

Ordinary Members of Council: Edward C. C. Baly; Augustus E. Dixon, M.D.; J. J. Dobbie, M.A., D.Sc., F.R.S.; Bernard Dyer, D.Sc.; Alfred D. Hall, M.A.; A. Lapworth, D.Sc.; J. E. Marsh, M.A.; E. J. Mills, D.Sc., F.R.S.; G. T. Moody, D.Sc.; W. J. Sell, M.A., F.R.S.; J. M. Thomson, LL.D., F.R.S.; J. Wade, D.Sc.

The proceedings then terminated.

PRESIDENTIAL ADDRESS.

Delivered at the ANNUAL GENERAL MEETING, MARCH 29TH, 1905.

By WILLIAM AUGUSTUS TILDEN, D.Sc., F.R.S.

MY first and most agreeable duty is to congratulate the Society on its continued growth and activity.

In offering my sincere thanks to my colleagues on the Council for their friendly co-operation in the administration of the affairs of the Society, I cannot refrain from expressing my regret that Professor Wynne is no longer able to retain the office of Senior Secretary. That regret will, I believe, be shared by every Fellow, but more especially by those who have taken part in the work of the Council and the various Committees. Dr. Wynne's devotion to the service of the Society, his care of detail and judicious handling of many difficult problems have been conspicuous throughout his tenure of office and deserve the warmest recognition. As a Vice-President, he will still be in a position to render much assistance, and we may hope that his distant residence will not prevent his frequent presence at meetings of the Council.

The chief events of the past year have been briefly referred to in the Report of the Council. One event not referred to, because not falling within the range of the operations of the Society, must afford gratification to all who are interested in the position and progress of science in England. I refer to the award of the Nobel Prize in chemistry to our distinguished Foreign Secretary, Sir William Ramsay. I believe the Society will permit me to offer, on its behalf, an expression of hearty congratulations on this occasion, and of good wishes for the progress of the remarkable investigations in connection with radioactive substances which have recently been associated with his name.

Another event, to which I refer with some personal satisfaction, is the issue of the first volume of Annual Reports on the Progress of Chemistry. The thanks of the Society are due to the several writers who have undertaken the heavy task of selection and compilation, and who have displayed great skill and judgment in the work entrusted to them. I believe these reports will be found interesting, instructive, and of great practical value to chemists of all classes.

The delivery of a Faraday Lecture by Professor Ostwald was an occasion of much interest, but the circumstances connected with it will provide a subject for serious consideration by future Councils. That so long a period has elapsed since the last lecture is due, not to inactivity on the part of the Council, but to the difficulty of finding foreign chemists, of the eminent scientific rank to which we have been accustomed in our Faraday Lecturers, who are willing or able to undertake the office. There are two directions in which some relief might be found from this difficulty. On the one hand, the invitation to lecture might be extended, as indeed it has been on one occasion, to eminent foreign physicists, and, on the other hand, a British chemist might from time to time be asked to assist. So long an interval as fifteen years ought not again to be allowed to elapse, and although it may not be possible to sustain the recurrence of the lecture at so short a period as three years, the lecture ought to be given *vivâ voce* often enough to be of some practical use for the purpose of marking the progress of science as well as keeping green the memory of Faraday.

Other events of the year are connected with questions concerning which there is room for wide differences of opinion. Taking advantage of the privilege usually accorded to the President, I will venture to make on these topics a few remarks which, of course, represent only my personal view of these matters.

The Council has received two memorials, of which one relates to the admission of women to the Fellowship. Whatever views each of us may hold as to its desirability, we have the opinion of Counsel learned in the law that the terms of the Charter preclude such admission. Participation in the government of the Society, or, to put it technically, to become corporators, appears to be the only privilege enjoyed by Fellows which cannot legally be extended to women. They might be allowed to attend the scientific meetings, to use the Library, to receive the publications of the Society, and to introduce friends to the scientific meetings, but they could not vote at a general meeting nor become members of the Council. It has been suggested that the best thing to do would be to test the validity of this legal opinion by putting up the name of a lady for election, and, if possible, getting her elected and admitted as a Fellow, letting those who object take any action they think proper. I think, however, it would be difficult to find a lady willing to be the *corpus vile* of such an experiment, which, whether successful or not, would hardly conduce to harmony in the Society. The number of women desiring admission is but small, and I fail to see any cogent reason, beside the legal one, for excluding them. Some of them are doing admirable scientific work, and

all the memorialists are highly qualified. To deprive them of such advantages as attach to the Fellowship simply on the ground that they are not men seems to be an unreasoning form of conservatism inconsistent with the principles of a Society which exists for the promotion of science. If, after further consideration, the moderate proposal of the Council to admit women as Associates does not prove acceptable to the Society, the best course will be to take steps for obtaining a Supplemental Charter. In any case, I think such a move must be made before long in order to get rid of some other anomalies to which I need not specifically refer.

Another memorial presented to the Council set forth the desire of the memorialists to return to the use of the word "radical" in the publications of the Society in place of the word "radicle," which has for many years been established in our pages. The contention that "radical" was the original spelling must be admitted, and the change to "radicle," which appears to have been made under the editorial influence of Mr. Henry Watts, had little to recommend it forty years ago, except grammatical form. But since that time, changes of theory in respect to chemical constitution and the formulation of chemical compounds have imposed a change on the connotation of this word, and that which is now understood, even by those who continue to use the "radical" form, is certainly not that which was implied in the system of Lavoisier and De Morveau when they distinguished between the "*radical*" and the "*principe acidifiant*" of acids. Nor, save in rare cases, is the meaning that which was understood by Liebig and Wöhler. C_2H_3O or $C_2H_3O_2$ may be the "radical," that is, the fundamental part of acetic acid, but when the formula for this compound is dissected in modern fashion, and it becomes $CH_3{\cdot}CO{\cdot}OH$, the "radical" is divided into several "radicles," no one of which has the right to be considered characteristic and fundamental. This becomes still more obvious if we take the constitutional formula of a more complex compound such as glucose or uric acid. Happily the question requires very little debate as the word has for some time been growing less and less familiar, until it has now practically disappeared. In its place we meet with nucleus or group or ion, according to circumstances. Hence, I think the Council was right in deciding to make no change, but to instruct the Editor to avoid the use of the word.

With regard to the occasion on which the Bye-Laws were submitted by the Council to an Extraordinary General Meeting, I desire to make only one remark. It seems to me unfortunate that when a subject so important is brought up for the judgment of a body numbering upwards of 2,700 members, the appointed meeting should be attended by not more than forty-five. The consequence is that on the occasion referred

to twenty-three Fellows were sufficient to form the majority which determined the fate of a matter which had been prepared with deliberation by the *larger number* of other Fellows who form the Council.

During the last year, the question of the selection of the standard for atomic weights has become more urgent. The Atomic Weight Committee of the German Chemical Society (Landolt, Ostwald, Wallach) has issued a circular addressed to the members of the Great International Committee on Atomic Weights in which they urge very forcibly their view that only one table of atomic weights should be issued, namely, the table in which all are referred to O = 16 as the basis. The International Committee (Clarke, Moissan, Seubert, Thorpe) has, however, issued two lists of atomic weights, the one referred to O = 16, the other to H = 1, and an explanation of their position is given fully in their annual report, which has been printed in our Journal (*Proc.*, 1905, 21, 2). The argument against a double table is based chiefly on the undesirability of a double standard and the confusion which is apprehended in molecular weights, in the strength of standard solutions, and in the values of physical constants in which atomic weights are involved. This argument would be more weighty if it were certain that the issue of a single table by the International Committee would be followed by uniformity in the atomic weights generally used. The values which receive the official sanction represent the nearest approach to accuracy which, in the present state of knowledge, is possible, but even under O = 16 as the standard the great majority of the atomic weights contain fractions. For all ordinary purposes, the chemist will continue to use whole numbers, and thus a double system will be perpetuated, the one employed for purely scientific purposes, the other for everyday work, and there can never be assurance that the values given in the table are permanent. Moreover, although the values in the oxygen scale approach in many cases to whole numbers, they are not equally near to whole numbers. Thus, there can be little doubt that everyone will adopt 80 in lieu of 79·96 for bromine, but in the case of aluminium some chemists will use 27 and some 27·1. Other similar questions arise. Is barium to be 137 or 137·5? Is chlorine to be 35·5? Is calcium to be 40 and magnesium 24?

The establishment of a general agreement as to the round numbers to be chosen for common use and the publication of such a conventional list of atomic weights would do more, I believe, toward securing uniformity in all really practical data than the suppression of the table of atomic weights calculated on the hydrogen scale.

For my part, I hope the International Committee will not deprive us of the hydrogen standard; without it or some other unit, atomic weight

cannot be defined, and for some theoretical purposes it is almost indispensable.

Turning now to a different subject, I venture once again to make an appeal to authors of papers in regard to the preparation of their manuscript and the condensation of the matter they wish to communicate. In addition to the significant facts mentioned by the Treasurer, I may point out that the Transactions for the past year contain 1,761 pages, not including the index, and I am informed that the cost of this part of our work has been £951, in addition to salaries and office expenses. This corresponds to approximately eleven shillings a page. But even assuming that the Society had unlimited funds available for the expenses of publication, it would still be undesirable to give unlimited license to writers of papers. The bulk of scientific literature is already enormous, and long papers are, as a rule, less likely to be read than those of moderate length. If, in compiling papers, authors would bear this in mind, they would be less frequently content to send in undigested extracts from note-books, inordinately detailed descriptions of familiar or insignificant operations, repetitions of the same statement in the modern, but not always clearly defined, division into theoretical and experimental, beside other forms of prolixity. I am unable to suggest any general rule which could be usefully applied in such cases, and although the action of the Publication Committee is frequently misunderstood, we must trust to time and common sense to surmount these difficulties.

The Reports just issued by the Society show how vast is the field of inquiry occupied by chemists, and how impossible it will be in the future for any President to review, in the fashion of former days, the progress of the year. In place of any such attempt, I venture to offer a summary of the present state of knowledge of a subject to which I have devoted attention for some years.

The Relation of Specific Heat to Atomic Weight in Elements and Compounds.

"The atoms of all the elements have exactly the same capacity for heat." * In these terms the important generalisation known to every student of chemistry as the "Law of Dulong and Petit" was enunciated in 1819. An examination of thirteen of the solid elements by the method of cooling gave results which are embodied in the following table :

	Specific heats.	Atomic weights (O=1).	Atomic weight × specific heat.
Bismuth	0·0288	13·30	0·3830
Lead	0·0293	12·95	0·3794
Gold	0·0298	12·43	0·3704
Platinum	0·0314	11·16	0·3740
Tin	0·0514	7·35	0·3779
Silver	0·0557	6·75	0·3759
Zinc	0·0927	4·03	0·3736
Tellurium	0·0912	4·03	0·3675
Copper	0·0949	3·957	0·3755
Nickel	0·1035	3·69	0·3819
Iron	0·1100	3·392	0·3731
Cobalt	0·1498	2·46	0·3685
Sulphur	0·1880	2·011	0·3780

The difference between the lowest and the highest product of the specific heat by the atomic weight in this table is only about 4 per cent., which, considering the uncertainty of many of the atomic weights, and the undoubted impurity of some of the materials, represents an insignificant deviation from a constant value, and seems to justify the statement of the authors. Regnault, who, a few years later, added largely to the existing knowledge of specific heats, also accepted the statement as representing a physical law, and on this assumption proposed changes in certain of the atomic weights so as to bring them into harmony with it. Regnault's experiments were made by the method of mixture, and were conducted chiefly between the temperature of the air and that of boiling water, and although the increase of specific heat at higher temperatures was known to him, and even to Dulong and Petit, it seems to have been generally assumed that the difference was insignificant.

* "Les atomes de tous les corps simples ont exactement la même capacité pour la chaleur." *Ann. Chim.*, 1819, **10**, 405.

Kopp, in his well-known memoir (*Phil. Trans.*, 1865, **155**, 71), expressed the view that "the specific heat of a solid body varies somewhat with its temperature, but the variation of the specific heat with the temperature is very small, provided the latter does not rise so high that the body begins to soften. Taking the numbers obtained by Regnault for lead, by Dulong and Petit, by Bede and by Byström for the specific heats of several metals at different temperatures, the conviction follows that the changes of specific heat, if not of themselves inconsiderable, are yet scarcely to be regarded in comparison with the discrepancies in the numbers which different observers have found for the specific heat of the same body at the same temperature."

The low specific heat of the element carbon had attracted the notice of Regnault, who proposed to double its atomic weight so as to bring it into line with the rest of the elements which conform with the law of Dulong and Petit. By Kopp, carbon and the allied elements, boron and silicon, were frankly regarded as exceptions to the law, concerning which he stated deliberately that it is not to be regarded as universally valid. Kopp's conclusion was supported by the results of experiments made by other physicists, and it was, moreover, established that the several allotropic modifications of carbon have different specific heats.

A consideration of the results of all the previous researches on the specific heats of carbon, boron, and silicon led H. F. Weber, in 1872 (*Phil. Mag.*, 4, 49, 161 and 276), to the conclusion that the specific heats of the different modifications of these three elements increase with rise of temperature more quickly than those of any other known substance. About the same time, experiments by Dewar on the mean specific heat of gas carbon, graphite, and diamond between 20° and the boiling point of zinc (at that time erroneously taken to be 1040°) and of the oxyhydrogen blowpipe flame (estimated at 2100°) led to a similar conclusion.

The following tables contain the results of Weber's experiments together with a few estimations of the specific heat of carbon made by myself. To these values of the mean specific heat have been added the product obtained by multiplying the mean specific heat by the range of temperature in each case. This product, represented by Q, expresses the total amount of heat absorbed by the substance in passing from the lower to the higher temperature, and is convenient for the purpose of graphical representation and comparison. In the curves given later (pp. 558—563), the higher absolute temperatures above 0° and the lower absolute temperatures below 0° are used as abscissæ.

From C°.	To C°.	Mean specific heat.		Q.	Absolute temperature, C°.
		Diamond.			
−182·5	15	0·0473	(Tilden)	9·3	91
−79·7	0	0·0720	(Weber)	5·7	193
−21·25	0	0·0953	,,	2·0	252
+21·4	0	0·1128	,,	2·4	294
45·3	0	0·1228	,,	5·5	318
71·2	0	0·1339	,,	9·5	344
99·8	0	0·1461	,,	14·6	373
180·2	0	0 1799	,,	32 3	453
232·0	0	0·2006	,,	46·5	505
282·0	0	0·2187	,,	61·6	555
322·0	15	0·2289	(Tilden)	70·3	595
417·0	15	0·2557	,,	102·8	690
528·5	22·3	0·3016	(Weber)	155·0	801
702·0	22·2	0·3374	,,	237·8	975
		Graphite.			
−182·5	15	0·1027	(Tilden)	20·2	91
−79·8	0	0·1219	(Weber)	9·7	193
−21·4	0	0·1442	,,	3·0	252
+21·6	0	0·1605	,,	3·4	294
99·0	0	0·1904	,,	18·8	372
178·0	0	0·2187	,,	38·9	451
225·3	0	0·2350	,,	52·8	498
273·2	0	0·2508	,,	68·4	546
557·2	22	0·3251	,,	177·3	830
742·6	22·4	0·3574	,,	260·7	1015

True specific heats calculated by Weber from the foregoing means are contained in the table on p. 554, together with the true atomic heats, to which reference will be made later (p. 556).

Weber, then, proved that the specific heat of carbon increases, at first very rapidly, with rise of temperature until a point is reached at which the increase is very slow. The specific heat of graphite is throughout somewhat greater than that of diamond, but at 600° and upwards the difference between them, as well as other forms of black carbon, is small, and the specific heat, if not constant, increases very slowly with further rise of temperature.

That the temperature exercises only an insignificant influence on the magnitude of the specific heats of the elements, and that this influence may be overlooked without introducing any serious error into the determination of the specific heat, is an idea which Weber regarded as no longer tenable. The specific heats of the solid elements are not affected to the same extent by temperature, but Weber believed that for every element a temperature could be found at which

the variation of the specific heat with changing temperature would be unimportant.

Another case in which the influence of temperature on specific heat has been carefully investigated is that of glucinum (beryllium). Humpidge, in 1885, showed (*Proc. Roy. Soc.*, **39**, 1) that the true specific heat of this metal increases from 0·3756 at 0° to 0·6206 at 500°, and that at the latter temperature it remains practically constant.

Temperature, C°.	True specific heat.	Atomic heat. S. H. × A. W. C=12.	Temperature, C°.	True specific heat.	Atomic heat. S. H. × A. W. C=12.
	Diamond.			*Graphite.*	
−50·5	0·0635	0·76	−50·3	0·1138	1·36
−10·6	0·0955	1·14	−10·7	0·1437	1·72
+10·7	0·1128	1·35	+10·8	0·1604	1·92
33·4	0·1318	1·58	61·3	0·1990	2·38
58·3	0·1532	1·83	138·5	0·2542	3·05
85·5	0·1765	2·11	201·6	0·2966	3·55
140·0	0·2218	2·66	249·3	0·3250	3·90
206·1	0·2733	3·27	641·9	0·4454	5·34
247·0	0·3026	3·63	822·0	0·4539	5·44
606·7	0·4408	5·28	977·9	0·4670	5·60
806·5	0·4489	5·38			
985·0	0·4589	5·50			

About eight years ago I began an investigation in which the law of Dulong and Petit was at the outset assumed to be valid. On comparing pure cobalt and nickel with each other it was found (Bakerian Lecture, *Phil. Trans.*, 1900, **194**, 233) that the specific heats of both metals increase with rise of temperature, that of nickel increasing the more rapidly, so that as the temperature rises the atomic heats of the two metals diverge more and more from each other. Later, I determined through a long range of temperature the specific heats of aluminium, silver, and platinum, and found that while the specific heats of silver and platinum increase but slightly with rise of temperature, that of aluminium rises very rapidly (*Phil. Trans.*, 1903, **201**, 37). The following table gives the true specific heats of the metals already mentioned together with the specific heats of tin and tellurium for successive temperatures on the absolute scale. The values given by Violle for platinum from 0° to 1000° and 1177° (*Compt. rend.*, 1877, **85**, 543, also *Phil. Mag.*, [v], **4**, 318) are used in the calculation for the higher temperatures.

True Specific Heats.

t abs. C°.	Aluminium.	Nickel.	Silver.	Platinum.	Tin.	Tellurium.
100	0·1226	0·0575	0·0467	0·0275	0·0462	0·0462
200	0·1731	0·0878	0·0528	0·0293	0·0504	0·0471
300	0·2053	0·1054	0·0558	0·0311	0·0548	0·0480
400	0·2254	0·1168	0·0572	0·0328	0·0596 ?	0·0489
500	0·2384	0·1233	0·0581	0·0344	—	0·0498
600	0·2471	0·1275	0·0587	0·0358	—	0·0507
700	0·2531	0·1301	0·0590	0·0372	—	0·0516
800	—	0·1321	—	0·0385	—	—
900	—	0·1338	—	0·0397	—	—
1000	—	—	—	0·0409	—	—
1100	—	—	—	0·0421	—	—
1200	—	—	—	0·0432	—	—
1300	—	—	—	0·0442	—	—
1400	—	—	—	0·0452	—	—
1500	—	—	—	0·0461	—	—

From these results, the following atomic heats are calculated (*Phil. Trans.*, 1903, **201**, 38, and 1904, **203**, 143):

t abs. C°.	Aluminium, Al=26·9.	Nickel, Ni=58·3.	Silver, Ag=107·12.	Platinum, Pt=193·3.	Tin, Sn=118·1.	Tellurium, Te=126·6.
100	3·30	3·35	5·00	5·31	5·46	5·85
200	4·66	5·12	5·65	5·66	5·95	5·96
300	5·52	6·14	5·98	6·01	6·47	6·08
400	6·06	6·81	6·13	6·34	7·04 ?	6·19
500	6·41	7·19	6·22	6·64	—	6·30
600	6·65	7·43	6·29	6·92	—	6·42
700	6·81	7·58	6·32	7·19	—	6·53
800	—	7·70	—	7·44	—	—
900	—	7·80	—	7·67	—	—
1000	—	—	—	7·90	—	—
1500	—	—	—	8·91	—	—

About the same time, a series of experiments by U. Behn on the specific heats of the metals, graphite and some alloys at low temperatures, supplied an independent series of data (*Wied. Ann. Physik*, [iv], 1, 257).

As a result of all these researches, facts are now available for an examination of Weber's conclusion that the law of Dulong and Petit "may be accepted as binding in the case of all the elements" provided the specific heat of each is determined at such a temperature

that the variation of specific heat with change of temperature is insignificant.

According to Weber, the constant values for the specific heats of carbon, boron, and silicon are in round numbers 0·46, 0·50, and 0·205 respectively, and these numbers multiplied by the atomic weights 12, 11, and 28 are for carbon 5·5, boron 5·5, and silicon 5·8.

If we now take the true atomic heats of the other elements at temperatures at which they are increasing but slowly, we have the following numbers :

Aluminium at	700°	absolute	6·81
Nickel at	800	,,	7·70
Silver at	600	,,	6·29
Platinum at	1000	,,	7·90
Tellurium at	600	,,	6·42
Tin (doubtful)	400	,,	7·04
Glucinum......	773	,,	5 64

The extremes among these numbers are carbon 5·5, platinum 7·9, which stand toward each other nearly in the ratio 2 : 3. The approach to a constant applicable to all elements is therefore less obvious when the condition indicated by Weber is fulfilled, and the true specific heats are used, than when, according to the usual practice, the mean specific heat between 0° and 100° is multiplied by the atomic weight, and the elements carbon, boron, silicon, and glucinum are regarded as exceptions.

The conclusion is therefore inevitable that the statement of Dulong and Petit, in the uncompromising form in which it was originally enunciated, cannot be accepted, and the usual application of the specific heat in the choice of atomic weights, although serviceable, is only based on the recognition of a rough empirical rule applicable generally, within the usual limits of temperature, to the metals but not to the exceptional elements. Nor is it reasonable to expect anything more precise, for of the several states of matter the solid state is that of which we possess the least knowledge. Yet the law of Dulong and Petit assumes that in solids the relation of the atoms to one another is the same notwithstanding the great diversity of fusibility, tenacity, and other mechanical properties observed in bodies. Such properties as expansibility appear to have but little influence on specific heat. Comparing together lead and platinum, for example, the atomic weights and specific heats of which are near together, lead has a coefficient of expansion about ten times that of platinum. Nickel and nickel steel also have specific heats near together at successive temperatures, the latter being somewhat the greater notwithstanding its very small coefficient of expansion (*Phil. Trans.*, 1903, **201**, 40).

Specific heat is an affair of atoms, not of molecules. This is demon-

strated by the facts embodied in the law of Neumann, but it becomes much more obvious if the specific heats of a compound and of the elements of which it is composed are separately determined through a long range of temperature. It may thus be ascertained whether an element, the specific heat of which increases considerably with rise of temperature, retains this peculiarity in its compounds. With this object in view, I have made a number of determinations of the specific heats of some compounds of the elements aluminium, nickel, silver, tin, and tellurium, the atomic heats of which have already been given (p. 555). The specific heats of the compounds formed by combining these in pairs were determined at intervals from the boiling point of liquid oxygen to a temperature as high as possible without approaching the melting point of the compound. From the mean specific heats thus obtained, the true specific heats were calculated, as before, for intervals of 100° absolute, and from these the true molecular heats have been derived by multiplying by the respective molecular weights. These are contained in column B of the following table; column A contains the sum of the atomic heats of the separate elements which enter into these compounds.

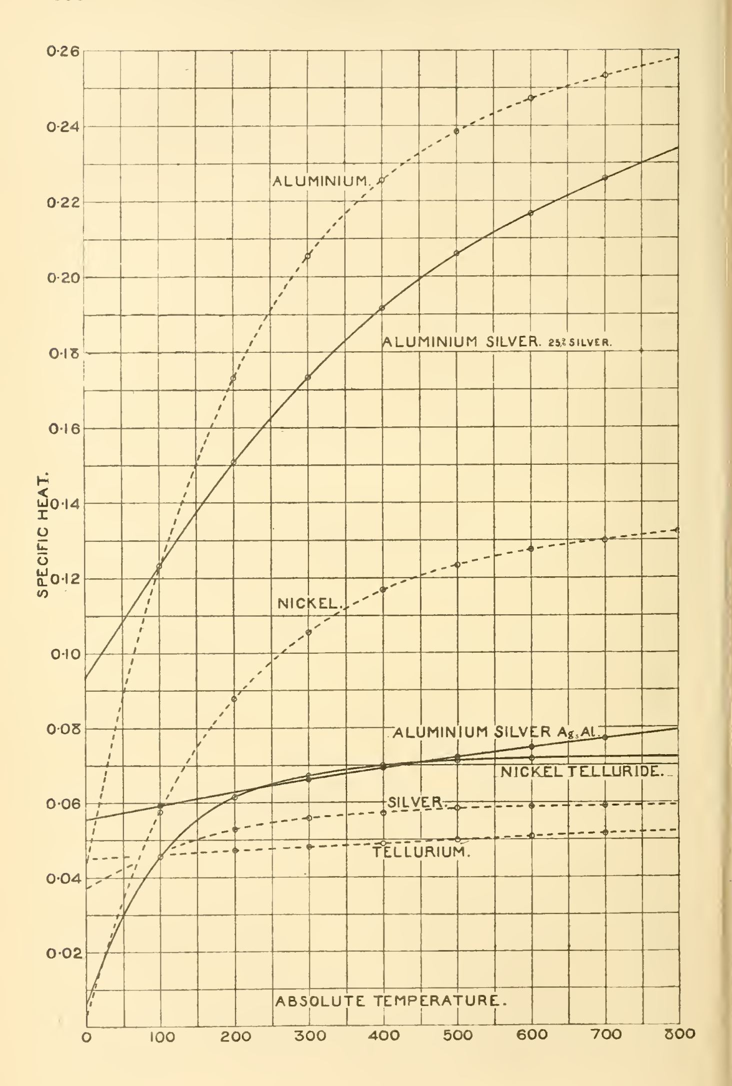
Molecular Heats of Compounds.

t abs. C°.	$SnTe_2$. A.	$SnTe_2$. B.	NiTe. A.	NiTe. B.	Ag_3Al. A.	Ag_3Al. B.	$AgAl_{12}$. A.	$AgAl_{12}$. B.
100	17·16	17·33	9·20	8·38	18·30	20·58	44·60	53·01
200	17·87	17·51	11·08	11·35	21·61	22·38	61·57	64·92
300	18·63	17·77	12·22	12·41	23·46	23·06	72·12	74·42
400	19·42	18·10	13·00	12·92	24·45	24·14	78·85	82·41
500	—	—	13·49	13·15	25·07	25·15	83·14	88·56
600	—	—	13·85	13·28	25·52	26·05	86·09	93·12
700	—	—	14·11	13·35	25·77	26·85	88·04	97·16
800	—	—	—	—	—	—	—	—

A = calculated from the atomic heats of the elements.
B = calculated from the observed specific heats of the compounds.

The aluminium silver alloy containing 24·9 per cent. of silver shows a greater difference between B and A than in the other cases, but even in this instance the differences are really small, the maximum being about 15 per cent. of the molecular heat at the lowest temperature, whilst the minimum difference is only 3 per cent. at 300°.

From the close concordance between the two columns of figures in each case, it is evident that Neumann's law is approximately exact, not only between the usual limits of temperature, but at all temperatures at which the materials remain solid.



SPECIFIC HEAT.
0·26
0·24
0·22
0·20
0·18
0·16
0·14
0·12
0·10
0·08
0·06
0·04
0·02
ALUMINIUM.
ALUMINIUM SILVER. 25% SILVER.
NICKEL.
ALUMINIUM SILVER Ag3Al.
NICKEL TELLURIDE.
SILVER.
TELLURIUM.
ABSOLUTE TEMPERATURE.
0
100
200
300
400
500
600
700
800

The graphic representation (p. 558) of the true specific heats of the elements and of the compounds of the same shows clearly the influence of the preponderating constituent in each case. The elements follow the dotted curves, the compounds the continuous curves.

Inasmuch as it might be thought that the force of affinity between the constituents of alloys and of compounds such as tellurides is too weak to produce much effect on their atomic heats, I have made a further attempt to trace the peculiarities of certain elements by studying the influence of temperature on the specific heat of some compounds in which the characteristic physical properties of the elements present have totally disappeared. Alumina was chosen for comparison with aluminium with the following results :

Mean Specific Heat of Alumina (Unpublished Experiments).

	15° to 100°.	15° to 195°.	15° to 315°.	15° to 420°.	15° to 510°C.
White corundum	0·2011	—	—	—	—
Sapphire	0·1993	—	—	—	—
Artificial Al_2O_3 (fused)..	0·2005	—	—	—	—
Sapphire	—	0·2195	—	—	—
,, ...	—	—	0·2311	—	—
,, ...	—	—	—	0·2400	—
,, ...	—	—	—	—	0·2472
Artificial Al_2O_3 (fused)..	—	—	—	—	0·2456
General mean	0·2003	0·2195	0·2311	0·2400	0·2464
Q =	17·0	39·5	69·3	97·2	121·9
At t abs......	373°	468°	588°	693°	783°

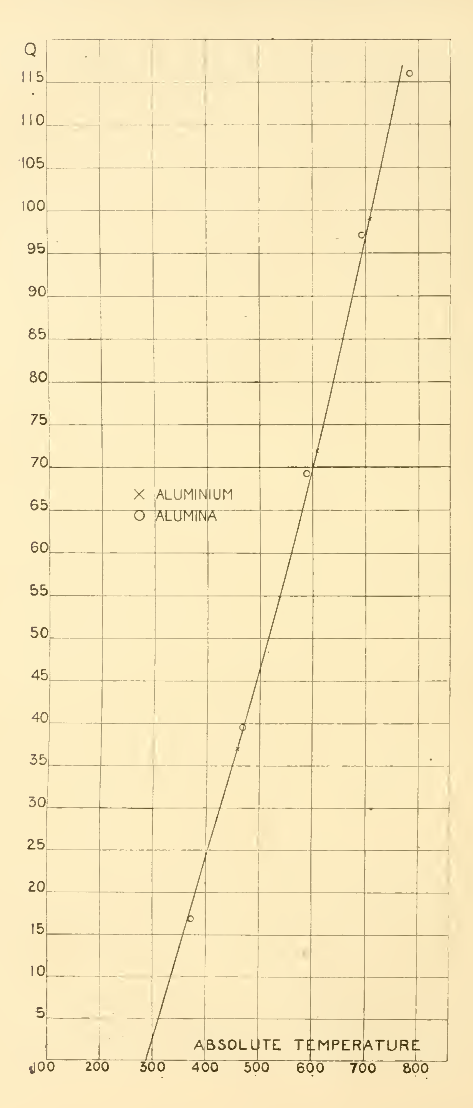
Mean Specific Heat of Aluminium.

15° to 185°	0·2189	whence $Q = 37·2$
15 to 335	0·2247	,, $Q = 71·9$
15 to 435	0·2356	,, $Q = 98·9$

When these are plotted as before, with Q as ordinates and the higher absolute temperatures as abscissæ, the curve shown on p. 560 is produced.

Since alumina consists of nearly equal parts of metal and oxygen, the close approximation of the two series of experimental results shows that oxygen in the solid form has a specific heat practically identical with that of aluminium.

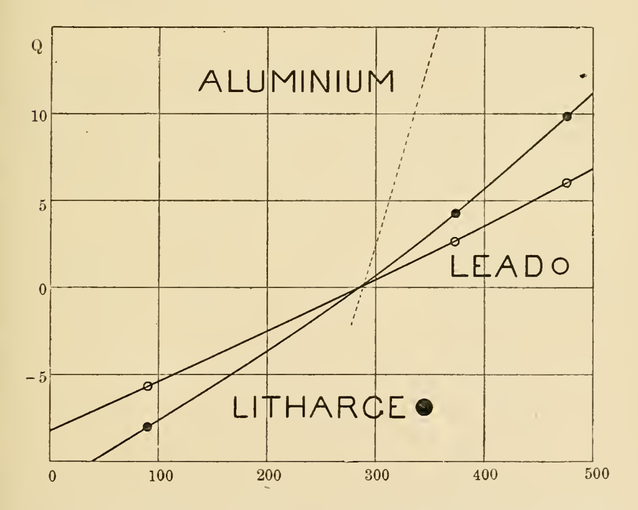
I have also made a few experiments on lead oxide (litharge) and lead, and the numbers and curves on p. 561 show that the specific heat of the oxide is in this case much greater than that of the metal.


Q
115
110
105
100
95
90
85
80
75
70
65
60
55
50
45
40
35
30
25
20
15
10
5
× ALUMINIUM
○ ALUMINA
ABSOLUTE TEMPERATURE
100
200
300
400
500
600
700
800

Mean Specific Heat.

	Lead oxide.		Lead.		
Temp. C.	S. H.	*Q.*	S. H.	*Q.*	Temp. abs.
– 182·5° to 15°	0·0403	7·96	0·0290	5·73	90·5°
15° to 100	0·0510	4·33	0·0309	2·63	373·0
15 to 203	0·0527	9·90	0·0320	6·02	476·0

The atomic heat of solid oxygen was estimated by Kopp, from observations of the specific heats of compounds containing this element, to be 4·0 (approx.) at temperatures from about 15° to 100°. If we



assume the specific heat of solid oxygen to be identical with that of aluminium, the atomic heat of oxygen at successive temperatures will be as follows :

$t°$ abs.	S. H. × 16.	=	Atomic heat.
100	0·1226		1·9
200	0·1731		2·7
300	0·2053		3·3
400	0·2254		3·6
500	0·2384		3·8
600	0·2471		3·9
700	0·2531		4·0

The values deducible from the specific heats of other oxides, using Regnault's numbers, may be set down for comparison, but it will be

observed that as the proportion of oxygen in the compound diminishes the estimated atomic heat for the oxygen increases. It may fairly be assumed that the most trustworthy results are deduced from those cases in which the oxygen forms a large proportion of the mass of the oxide.

Oxide.	Oxygen per cent.	A. H. (15° to 100°).
Al_2O_3	47·0	3·3
MgO	40·0	3·7
ZnO	19·7	3·9
HgO	7·4	4·7
PbO	7·1	5·0

The estimate I have suggested (*Phil. Trans.*, 1904, **203**, 148) for the atomic heat of *gaseous* oxygen is 2·7.

An attempt has been made to trace the specific heat of carbon in solid combination. For this purpose, two hydrocarbons, picene and ozokerite,* were chosen containing respectively a small and a large proportion of hydrogen. The choice is limited owing to practical difficulties. Picene has the formula $C_{22}H_{14}$ and contains 94·96 per cent. of carbon and 5·04 per cent. of hydrogen.

Mean Specific Heat of Picene (m. p. 364°).

Temp. C.	S. H.	*Q.*	*t*° abs.
−182·5° to 15°	0·1601	31·5	90·5
−95·3 to 15	0·1676	18·4	177·7
15 to 100	0·2829	24·0	373·0
15 to 210	0·3566	69·5	483·0

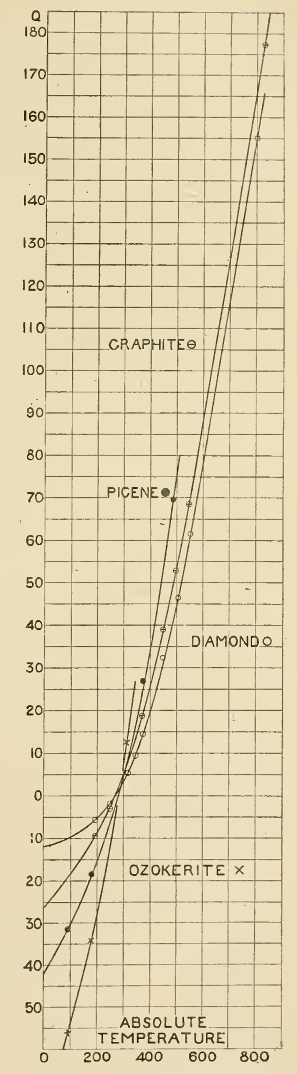
Mean Specific Heat of "Ozokerite" (m. p. 65°).

−182·5° to 15°	0·2846	56·0	90·5
−95·3 to 15	0·3114	34·3	177·7
15 to 40·7	0·4956	12·7	313·7

When the values of *Q* are plotted against absolute temperatures as in previous cases, the hydrocarbons are found to yield curves similar in character to those of graphite and diamond at the higher temperatures. The specific heat of hydrogen is much greater than that of carbon at all temperatures, nevertheless the increase in the specific heat by rise of temperature which is characteristic of carbon is manifest in the specific heat of the compound notwithstanding the hydrogen which is associated with it. These data are insufficient for any probable estimate of the atomic heat of solid hydrogen, which is best deduced from the specific heat of ice. Kopp put the number 2·3 for the atomic

* Natural ozokerite was heated with oil of vitriol for some hours, then washed and distilled and the solid distillate crystallised from alcohol. The white product melted at about 65° and consisted, presumably, of a paraffin approximating to $C_{28}H_{58}$, which contains 85·27 per cent. of carbon and 14·73 per cent. of hydrogen.

heat of hydrogen, but if we assume from my experiments that the atomic heat of solid oxygen a few degrees below 0° is approximately 3, the value for hydrogen comes out about 2·7. Thus the specific heat of ice from − 78° to 0° is 0·47, and therefore the molecular heat is 8·46. Subtracting 3 for the oxygen, half the remainder, 5·46, is 2·7, the atomic heat of solid hydrogen.



Conclusions.

1. The influence of temperature on the specific heats of many elements and compounds is much greater than was formerly supposed.

2. There appears to be no one condition or set of conditions under which the law of Dulong and Petit is true of all the elements.

3. The nearest approach to a constant available for practical purposes is found by taking the mean specific heats of metals between the freezing and boiling points of water, recognising glucinum, boron, carbon, and silicon as exceptions, together with hydrogen, oxygen, nitrogen, and perhaps chlorine in the solid form.

It is possible that the atomic heats of elements in the gaseous state may be equal, direct experiment on the gases having led to the value 2·4 for hydrogen, 2·5 to 2·7 for oxygen, and 2·6 for carbon (in carbon dioxide).

4. The independence of each atom in an element or compound must be regarded as a fact of the utmost importance from the point of view of theory. That the molecular heat of a compound is the sum of the atomic heats of all the elements present is

in harmony with the results of observations on other additive properties, such as specific volume and specific refraction. Such independence suggests the idea that chemical combination results from the mechanical fitting together of atoms, so that a section through a mass would exhibit, if the atoms were visible, a certain tactical arrangement probably corresponding with the closest approximation possible under prevailing conditions. It has yet to be shown that chemical combination results, *in all cases,* from the existence of electric charges resident on the atoms or in electrons associated with them. The molecules of carbon compounds, especially, may be regarded as being probably formed by the adjustment of the constituent atoms to one another in respect to space, and it is noteworthy that the binary compounds of carbon, the hydrides, chlorides, and oxides, when in the liquid state, are not electrolytes, and no case is known of the electro-deposition of carbon from such compounds in the elemental form.

OBITUARY NOTICES.

FREDERICK AUGUSTUS ABEL.

BORN JULY 17TH, 1827; DIED SEPTEMBER 6TH, 1902.

THE sudden death of Sir Frederick Abel on September 6, 1902, at his residence, Whitehall Court, London, S.W., at the age of seventy-five years, removed from the English scientific societies one of their most distinguished and energetic representatives. Almost every branch of Technical Science had been enriched by his labours, and he became in turn the active official head of many important organisations during the latter part of the last century.

Born in London on July 17th, 1827, eldest son of the late J. L. Abel, of Kennington, a music master of German descent (whose father is said to have been Court Miniature Painter to the Grand Duke of Mecklenburg Schwerin), the subject of this memoir enjoyed the advantage of home training in two languages, his mother being English. At the age of fourteen he went to Hamburg on a visit to his uncle, A. T. Abel, a mineralogist and pupil of Berzelius, and probably to this circumstance may be ascribed his leaning towards scientific pursuits. Electing to become a chemist, young Abel commenced his studies in 1844 under Dr. Ryan at the Royal Polytechnic Institution; but, not finding this course of instruction acceptable, he changed over in the following year (October 1845) to the newly-founded Royal College of Chemistry, which, starting on the approved Giessen system with a pupil of the illustrious Liebig as the Professor, offered greater advantages. Abel was one of the twenty-six original students who began work in the temporary laboratories at George Street, Hanover Square, and migrated with the Professor, Dr. A. W. Hofmann, a year later, into the specially-erected buildings in Oxford Street, of which the foundation-stone had been laid by the Prince Consort in June 1846. So apt was he as a pupil that he was speedily elected an assistant, having for colleagues E. C. Nicholson, T. H. Rowney, and C. L. Bloxam, and being joined later by Dr. David S. Price, fresh from Professor Erdmann's laboratory at Leipzig. Here he spent five more years, teaching in the laboratory and doing some original work on his own account. He likewise assisted the Professor in some of his important

early researches, *e.g.* "Volatile Organic Bases." Abel was elected a Fellow of the Chemical Society of London in 1848, and read the following papers at meetings of that body :—

1847.	F. A. Abel.	"Products of the Oxidation of Cumol by Nitric Acid."
1848.	Abel and Rowney.	"Mineral Waters of Cheltenham." "Water from Artesian Wells, Trafalgar Square."
1849.	Abel and Nicholson.	"On Strychnine."

In 1851, Abel left the College to become Demonstrator of Chemistry at St. Bartholomew's Hospital under Dr. John Stenhouse; and when, two years later, the post of Lecturer on Chemistry at the Royal Military Academy, Woolwich, became vacant by the retirement of Michael Faraday (who had held it since 1829), Abel applied for it and was duly elected. This was the turning-point in his career, and marked the commencement of a long period of active service at Woolwich as the Scientific Adviser to the War Office, almost immediately resulting in his definite appointment as Chemist of the War Department, with official residence at Woolwich Arsenal, about the year 1854, when all the Government resources were being strained to their utmost in preparation for the great Russian war. At this time also his scientific reputation and influence were doubtless strengthened by the joint publication of a *Handbook of Chemistry* by Abel and Bloxam, with a Preface by Dr. A. W. Hofmann (724 pages), issued from the well-known press of John Churchill, London, in 1854.* This quickly ran through two editions, but when later a third was required, Abel, "not having leisure to devote to its preparation," as stated in the Preface, the work was reproduced in a somewhat different form by Charles L. Bloxam alone.

To enumerate the activities of the thirty-four years (1854–1888) during which Sir Frederick Abel retained his position at Woolwich Arsenal is no light task, inasmuch as it covers a period of great reforms in the Army and alterations of military equipment. The cast-iron ordnance and bronze field guns were superseded, breech-loading arms of greater precision were introduced, and new percussion fuses provided; also torpedoes, submarine mining, and blasting materials—even the black gunpowder in common use had to be changed—all demanding careful study and innumerable experiments.

The Navy also underwent a crucial change from the time-honoured "wooden walls" to iron ships and armour-plating. Chilled shot and

* The prime motive for the appearance of this work was the want of a suitable text-book to put into the hands of the cadets studying at the Royal Military Academy, who would find the Waltham Abbey processes for the purification of saltpetre and manufacture of gunpowder fully described, together with other details of professional interest.

steel shells were introduced, and then began the interminable contest between means of attack and defence. Trials were constantly made in Woolwich Marshes and at Shoeburyness of new schemes and constructions, all of which were supervised by military committees, on which Sir Frederick Abel invariably found a place.

As juror or British representative he was sent to do duty at the Paris and Vienna Electrical Exhibitions of 1881 and 1883; also he was Chief of the Executive of the International Inventions and Music Exhibition held in London in 1885; Member of the Ordnance Select Committee; of the Royal Commission on Accidents in Coal Mines; Expert for Petroleum Legislation, Submarine Defences, and Smokeless Powders; and until cut off by death he was for many years President of the Explosives Committee.

The lamentable accident at Messrs. Prentice's Stowmarket factory brought to light a hitherto unsuspected property of gun-cotton, showing that even in the form of moist pulp, and under water, it could be fired by detonation or extreme compression. Working on this basis, and with the happy collaboration of one of his assistants, Edwin O. Brown (who devised and carried out a special series of experiments, for which he was rewarded by the Government), Abel was driven to the conclusion that his first opinion as to the cause of the Stowmarket disaster would have to be modified; and as a final outcome of this inquiry most important results followed, which were immediately put to practical use in submarine and torpedo warfare. Then, again, as to the old form of gunpowder, working with Sir Andrew Noble on grains of enormous size, "pebble powder," it was found that the rapidity of ignition and pressure under which it was fired, exerted a vast influence upon the expansive force generated, and that even the products of combustion were variable under these different conditions. The powder had therefore to be specially prepared when the huge chambers of the 81-ton gun required to be supplied with ammunition, charges of "prism powder" being the result.

From 1868 to 1875, Abel devoted much of his time to the investigation of gun-cotton, publishing his results in the *Philosophical Transactions* of the Royal Society, and delivering lectures on special points at the Royal Institution, London, and Royal Artillery Institution, Woolwich. He was elected President of the Chemical Society for 1875–7, and during the tenure of this office he invited the Fellows to Woolwich on March 14, 1876, to witness a series of practical demonstrations in the Royal Arsenal. About four hundred members attended, and they were favoured with an ever-memorable programme of great scientific interest. Two rounds were fired from the 81-ton gun, called at that time "The Woolwich Infant." A grand series of gun-cotton experiments were displayed, showing the extraordinary difference in the

destructive effects according to the mode of ignition and confinement of the charges—sometimes burning slowly away or, if detonated, exploding with terrific violence. Torpedoes were launched in the Military Canal; the 40-ton steam-forging hammer was set in action, and the whole of the workshops and gun factories were open for inspection.

In September 1877, Abel was President of Section B (Chemistry) at the Plymouth meeting of the British Association; in 1881 and 1882, President of the Institute of Chemistry. The following year, 1883, he succeeded Sir Henry Roscoe as President of the Society of Chemical Industry, served at the Vienna Exhibition, as already mentioned, and was knighted. Then we find him busy on "Dangerous Dusts," Steel Testing, Nitro-Glycerine and Cordite, and helping the cause of Technical Education whilst on the governing body of the City and Guilds of London Institute and as Prime Warden of the Goldsmiths' Company; filling up his time by serving as Chairman of the Society of Arts, and President of the Institution of Electrical Engineers; Member of the Board of Managers, Royal Institution, and of the Council of the Royal Academy of Music. He was also Chairman of the British Committee in promotion of the Hofmann Testimonial, 1888, which added a considerable sum—about £270—to the International Fund.

Another subject upon which Sir F. A. Abel was consulted took the form of a reference touching the safety of Petroleum for storage and use as an illuminant in domestic lamps. In 1868, investigations led to the adoption of an Open-Test apparatus with the limit of 100° F. as "flash point"; but it was found later that more precise results could be obtained by the use of Abel's Close-Test apparatus and substitution of 73° F. (instead of 100°). This standard was legalised in 1879, and has ever since been adopted.

Somewhat akin to the above was an experimental inquiry undertaken at the request of the Home Office, 1880, into the question of Colliery Explosions and the influence of Coal-dust as one of the causes. The report was presented in June 1881, and went to show that the finely-divided particles suspended in air were a source of danger similar to that occasionally experienced in flour-mills. A lecture was delivered at the Royal Institution in April 1882 on "Dangerous Dusts," in which, after reviewing the Reports of Faraday and Lyell, 1845; Rankin and Macadam, 1872 (referring to the lamentable accident at the Tradeston Flour Mills, Glasgow, when several persons were killed), and to the later report of Marreco and Morison on Coal-dust dangers at Seaham Colliery, Durham, Sir Frederick Abel described his own experimental results, and pointed to the fact that, although a mixture of two or three per cent. of fire-damp with air was not itself inflammable, it became explosive, or "a carrier of flame," as

soon as the particles of coal-dust were diffused through such an atmosphere, as the consequence, for instance, of using the ordinary gunpowder-blast for dislodging masses of coal. The merits of the quicklime system of mining, and of the dynamite and water-blast were discussed.

In 1883, Sir F. A. Abel was elected an Honorary Member of the Institution of Mechanical Engineers, in recognition of his having undertaken for their Research Committee on the Hardening of Steel a series of experiments on the condition in which the carbon exists in that metal. The isolation of the carbide, Fe_3C, believed to be dissolved throughout the steel, was held to be a step to the elucidation of this subject; but it remained for the late Sir W. Roberts-Austen to put the finishing touch to this inquiry by attacking the problem from the physical side. The subject of steel, and the influence of small additions of other metallic elements, such as manganese, nickel, cobalt, chromium, and aluminium, was referred to at Leeds in 1890, when Sir Frederick Abel was President of the British Association for the Advancement of Science, and again in the following year, when he was President of the Iron and Steel Institute.

It had been decided to commemorate the Jubilee of Her Majesty Queen Victoria's reign by the erection of a grand edifice at South Kensington, which was to be devoted to a permanent exhibition of the natural products and articles of commerce obtainable from India and the British Colonies. The Museum was to be a centre of inquiry and conference between merchants and manufacturers of the Empire. Imperfectly-known substances were to be brought to their proper uses and turned to profitable account; some ores and drugs might require to be analysed, or made the subject of research, for which a trained scientific staff and suitable laboratories were provided. Sir Frederick Abel was appointed the Organising Secretary, and for fourteen years he devoted himself to this work (1887 to 1901), ceasing from his labours only when the perfected scheme was placed under the direction of the Board of Trade, and part of the surplus buildings devoted to the needs of the London University.

Blest with good health and indomitable perseverance, Abel succeeded in accomplishing an amount of work—and that of a nature sometimes attended with personal risk—which would have appalled many a scientific professor placed in similar circumstances. It is not surprising that honours fell fast upon him both by Royal patronage and University preferment. He was made a Companion of the Bath in 1877, and promoted to Knight Commander of this Order in 1891; knighted in 1883, and made a Baronet in 1893 (after the opening of the Imperial Institute), while in 1901 he was created a Knight Grand Cross of the Victorian Order. Oxford conferred its D.C.L. in 1883,

and Cambridge its D.Sc. in 1888. He held the Albert, the Royal, and the Telford Medals, also the Bessemer Gold Medal, 1897. As already stated, he was made successively President of many of the learned Societies and Honorary Life Member of others.

Sir Frederick Abel was one of the six Past Presidents of the Chemical Society, "who had accomplished their Jubilee as Fellows," in whose honour a Banquet was given in London on November 11, 1898, at the Whitehall Rooms. There were to have been seven, but Lord Playfair died while the preliminary arrangements were being made, and the Festival was consequently postponed from an earlier date (June 9th). Of these six or seven distinguished men only Professor Odling survives. The chair was taken by Professor Sir James Dewar, and an illustrious company assembled, including Dr. H. T. Böttinger, Professor W. Ostwald, Lord Lister, P.R.S., Lord Chief Justice Alverstone, several statesmen and heads of scientific departments, together with about two hundred and fifty Fellows of the Chemical Society.

Socially, the late Sir F. A. Abel was doubly acceptable on account of his splendid musical talents. Not a vocalist himself, he was ever ready to play the accompaniments, and even train a band of singers, besides giving exquisite performances on the grand pianoforte at many of the earlier dinners and festivities of the Chemical Societies. To hear his rendering of "William Tell," "Oberon," "Der Freischütz," "Tannhäuser," and other choice operatic selections, generally played without music score, was always a great artistic treat.

As to Clubs, he was a member of the Athenæum, the Savage, and the Garrick, and in former times one of the prominent members of "The Bees"—a small fraternity of chemical students (chiefly Hofmann's pupils) to whose meetings Abel used to take his zither.

Sir Frederick was twice married, but died a widower without children. The Baronetcy is therefore extinct.

J. SPILLER.

LOBRY DE BRUYN.

BORN JANUARY 1ST, 1857; DIED JULY 27TH, 1904.

AT the early age of forty-seven the name of one of the youngest of the Honorary Foreign Members of the Chemical Society disappears from the list. Scarcely had his election been completed, in May last, than he was seized with illness which ended fatally on July 27.

Cornelis Adriaan Lobry van Troostenburg de Bruyn was born on January 1, 1857, at Leeuwarden, where his father, Nicholaas Lobry van Troostenburg de Bruyn, was a physician in practice. The boy was in



due time sent to the high school of the town (Hoogere Burger School), and subsequently for a year to the Gymnasium. In 1875 he entered the University of Leiden, and in 1883, while acting as assistant to Professor Franchimont, he produced his dissertation and obtained his doctorate. The subject of this thesis was the interaction of the three dinitrobenzenes with potassium cyanide in alcoholic solution, an investigation to which he several times returned, and of the results of which he published a *résumé* so recently as the spring of 1904 (*Rec. Trav. chim. Pays-Bas*, 23, 39).

About this time De Bruyn went to Paris and worked for a few months in the laboratory of Wurtz, and in that of Friedel, returning to Leiden in 1884, where he remained until the following year. Having been appointed Chemist to the Government Department of Marine, his official duties naturally brought before his notice new problems, especially those connected with the manufacture and properties of explosives, and to this work he devoted much attention during eleven years. During this period he began the study of methyl and ethyl alcohols in the character of solvents, which led him on to the isolation of hydroxylamine and of hydrazine. Neither of these bases had up to this time been obtained in a free state, owing probably to the use of water as the solvent. De Bruyn found that hydroxylamine hydrochloride dissolves in about six times its weight of absolute methyl alcohol, and that when mixed with the calculated quantity of sodium methoxide, also dissolved in methyl alcohol, sodium chloride is precipitated, and a solution of hydroxylamine is obtained. From this the alcohol may be distilled off under reduced pressure. It was soon found that hydroxylamine is not a gas, as had been previously supposed, but a crystalline solid which, although very explosive, can be distilled under a low pressure. This isolation of hydroxylamine was accomplished in 1891. Hydrazine, discovered by Curtius in 1887, was known in the form of hydrate, from which, however, it had been found impossible to remove the elements of water. De Bruyn succeeded in 1894 in applying the method adopted for the isolation of hydroxylamine. The hydrochloride boiled with a methyl-alcoholic solution of sodium methoxide and then fractionated under reduced pressure gave solutions containing as much as 92 per cent. of hydrazine. The dehydration was completed by contact with barium oxide. The free base, originally described as a gas, was found to be a liquid at common temperatures, although freezing into a solid which melts at 1·4°, and in the liquid state having nearly the same density as its hydrate N_2H_4,H_2O, a remarkably stable substance which boils constantly at 118·5°. The whole of the physical constants of hydrazine were determined by De Bruyn, and are described in a memoir published in 1896 (*Rec. Trav. chim.*, 15, 174).

In this year he was appointed to succeed Gunning as Professor in the

University of Amsterdam, having declined the position of State Chemist offered to him in 1895 by the Government of the Transvaal. In this connection it may be mentioned that in 1901 a chair was offered to De Bruyn in the University of Vienna, an invitation which, however flattering, did not disturb his devotion to the work which lay before him in his own fatherland. His duties in Amsterdam included the instruction of pharmaceutical students as well as students of pure chemistry, but over all he exercised the same stimulating and inspiring influence which carried them forward, and to which many of those, especially who are applying their chemistry to the purposes of the profession of medicine, will have reason to look back with thankfulness.

In the inaugural address delivered on assuming his professorial duties De Bruyn announced his intention of studying the phenomena which are attributed to atomic rearrangement, and in the pursuit of these inquiries he gradually turned in his later years to problems of physical chemistry. The sort of questions with which he occupied himself are indicated clearly by the titles of some of his most recent papers. "Do the Ions carry the Solvent with them in Electrolysis?" * This question cannot be studied by using purely aqueous solutions, but it can be done by means of solutions of an electrolyte, say, in mixtures of water and methyl alcohol. Then if one of the ions carried with it one of the solvents, this would be found out by the difference in the proportion of the two solvents at the cathode and the anode both by comparing them with each other and with the original solution. Experiments made with silver nitrate led to the conclusion that under the circumstances of the experiments no such transference of the solvent occurred. Another, "On the Variations of Concentration of Solutions and the Crystallisation of Dissolved Substances under the Influence of Centrifugal Force," † led to a very remarkable result. With the object of determining whether gravitation was competent to effect any separation of a solid from the liquid in which it was dissolved, Gay-Lussac had long ago placed in the cellars of the Observatory at Paris, where the temperature is practically constant, a tube, two metres long, containing a solution of salt, and after a time determined the concentration of the top and bottom layers of solution. The result was negative, as the force of gravity was insufficient to bring about any change which could be experimentally recognised. Quite recently (1895), Bredig, ‡ making use of centrifugal force, succeeded in partially separating two gases, hydrogen and hydrogen iodide, which have very different molecular weights. Bredig made use of a sealed glass tube, having a tap in the middle, each arm being 21 cm. long and filled with the mixture. Having whirled the tube

* *K. Akademie Wetenschappen te Amsterdam*, August 1903.

† *Rec. Trav. chim.*, 1904, **23**, 218.

‡ *Zeit. physikal. Chem.*, 17, 459.

about 2400 turns a minute for $1\frac{1}{2}$ to 3 hours, the apparatus was stopped and the tap closed. On analysing the contents of the two arms of the tube a difference of about 3 per cent. was observed. De Bruyn, in concert with R. P. van Calcar, submitted solutions of various salts and of sugar in water to centrifugal action in an apparatus devised so as to permit of the removal of small quantities of liquid at different distances from the centre during the process of centrifugation. When a saturated solution of Glauber's salt was employed, so great was the concentration towards the periphery of the whirling drum that about $\frac{3}{8}$ths of the dissolved salt separated in the solid crystalline state, having a liquid in the middle which contained only 5·54 per cent. of anhydrous sodium sulphate !

No mention has been made of De Bruyn's work in connection with carbohydrates. The first communication jointly with Franchimont on the amino-derivatives of the sugars was the outcome of his use of methyl alcohol as a solvent. The further study of these compounds, pursued with van Leent, and later with Alberda van Ekenstein, director of the Government sugar laboratory, resulted from his discovery of the transformations of the sugars under the influence of alkalis, and were continued appropriately in connection with his duties as scientific adviser to the Minister of Finance. But no department of chemistry escaped his notice, and the variety and extent of his experimental labours can only be estimated after inspecting such a complete list of his published memoirs as will appear in the completed volumes of the Royal Society Catalogue.

In 1884, De Bruyn married Maria Simon Thomas, daughter of H. E. Simon Thomas, Professor of Obstetrics and Gynæcology in Leiden. He leaves two sons and two daughters. Though personally known to but few English chemists, his great services to science have been fully recognised in this country, and his recent election as an Honorary Foreign Member of the Chemical Society may be regarded as an expression of the appreciation of his English colleagues. As to his personal qualities, we may well believe the statement of his friends, Professor Cohen and Dr. Blanksma,* that his only fault was his too great modesty. In the words of one who knew him best, "he was like all really good men, a very kind father and husband, of that calm Dutch temperament which is never out of tune." Peace be to his ashes ! Though the march of science must go forward, his comrades cannot but feel that the world has lost in Lobry de Bruyn an active and successful leader and a good man.

W. A. Tilden.

* *Chemisch Weekblad*, 1, 985.

EDWARD FRANKLAND.

Born January 18th, 1825; Died August 9th, 1899.

In his autobiography, which has recently been printed for private circulation, Frankland tells us that he had been to seven schools by the time he reached the age of seven years. In the eighth school, near Lancaster, he remained until he was twelve, and it was here that he began to take an interest in science and consult books at the Mechanics' Institute; here he made a voltaic pile and decomposed water and joined with his schoolfellows in the making of fireworks and other experiments. From the age of twelve to fifteen he attended the Lancaster Free Grammar School. As he wished to enter the medical profession, his stepfather, acting on advice given by others, apprenticed him to a druggist for six years, in the belief that this would lead to the desired end. For the first two years of this apprenticeship he was the junior and had to do laborious and dirty work without holidays; in the third and fourth years he had one week's holiday in each year, and the fifth and sixth years were less trying. During his apprenticeship, Dr. James Johnson invited Frankland and some other druggists' apprentices to make use of a laboratory and small lecture-room which he had fitted up in a cottage, where they performed many chemical experiments and made rough analyses of waters.

In his twenty-first year, Frankland left Lancaster and went to London, where he was introduced to Dr. Lyon Playfair and commenced working in his laboratory in October 1845, under the direction of the assistant, Mr. Ransome. At the end of six months, Playfair appointed him lecture-assistant in the Civil Engineering College, Putney.

Kolbe was then assistant in Playfair's laboratory, and he and Frankland undertook an investigation suggested by the theory of Berzelius that acetic acid is a conjugate compound of methyl and oxalic acid, and on April 19, 1847, they read a paper at the Chemical Society "On the Chemical Constitution of Metacetonic (Propionic) Acid, and some other Bodies related to it," which was published in Chem. Soc. Mem., 1845—1848, 3, 386—391. They suspected that the nitriles, some of which had been prepared by other chemists, were in reality cyanides, and they prepared pure ethyl cyanide and acted on it with boiling solution of caustic potash, and obtained potassium propionate with evolution of ammonia.

In May 1847, Frankland went with Kolbe to Marburg and worked for three months in Bunsen's laboratory. Here they completed the work on the preparation of organic acids from the alkyl cyanides and

published a complete account of their researches in the *Annalen*, 1848, **65**, 288—304, under the title "Ueber die chemische Constitution der Säuren der Reihe $(C_2H_2)_nO_4$ und der unter dem Namen 'nitrile' bekannten Verbindungen." In this paper (April 15, 1848) they describe the use of the inverted condenser for digestions. They also attempted to isolate ethyl by the action of potassium on ethyl cyanide, when they obtained a gas having the composition of methyl; this gas, when acted on by chlorine, gave a compound which they supposed to be an isomeride of ethyl chloride. In the residue left after the evolution of the gas, they found the new base, cyanethine, of which they prepared the nitrate and platinichloride.

In the combustion of these compounds with oxide of copper, they employed a stream of oxygen evolved from potassium perchlorate placed in the posterior end of the combustion tube (Quart. Journ. Chem. Soc., 1849, 1, 60—74. Read February 7, 1848).

In August 1847, Frankland went to Queenwood College to teach chemistry, geology, and botany. It was here that his experiments on the isolation of the alcohol radicles* were commenced on April 10, 1848, in the attempt to remove the oxygen from ether by the action of potassium, but which yielded only hydrogen from the presence of water or of alcohol. On April 18, he prepared ethyl iodide for further experiments, this compound not having been hitherto used in chemical research. On April 21, he tried the action of potassium on ethyl iodide; no change took place in the cold, but when the iodide was heated near its boiling point, gas was evolved; this experiment was lost in consequence of the entry of water into the tube. On April 26, potassium and ethyl iodide were heated together in a sealed tube in an oil-bath; on opening the tube, a gas escaped which was found to be a mixture of methyl and hydrogen. Frankland appears to have been one of the first chemists to use sealed tubes in chemical research, and he tells us that, when he was working in Liebig's laboratory in 1849, Hofmann paid him a visit to learn the way of making these tubes and took a number of them back to London with him. On May 18, during the analysis of another quantity of the gas, the eudiometer exploded. In August, in attempting to prepare the radicle formyl by the action of potassium on chloroform, several serious explosions occurred, but apparently no important result was obtained.

He then returned to the isolation of ethyl, and on July 28, 1848, he sealed up a mixture of ethyl iodide and zinc in a glass tube and heated the tube to 300° F.; no action appeared to occur, but at 400° the zinc began to be slowly converted into iodide and the liquid ceased to boil.

In October 1848, Frankland, accompanied by Tyndall, went to Marburg and worked in Bunsen's laboratory. Here he isolated

* It should be noted that Frankland always spelt this word "radical."

chromium by electrolysis, but he does not appear to have published any account of its properties, which differed somewhat from those of the metal obtained by other processes. On February 18, 1849, he opened the tube in which, on July 28, 1848, he had heated the mixture of zinc and ethyl iodide. The tube was opened under water and some of the contents came in contact with the water, producing a violent effervescence. The gas was found to consist of ethyl mixed with methyl and ethylene. On March 2, he placed ethyl iodide and zinc in a tube from which the air was removed before sealing; after heating, the evolved gas was found to be a mixture of ethyl, methyl, and ethylene. When the sealed tubes were opened, a large quantity of gas rushed out, leaving a small quantity of volatile liquid in the tube; the vapour of this liquid was shown to be pure ethyl. The homogeneity and density of the gas were determined by observation of its rate of diffusion, this being the first application of this method. He endeavoured to combine ethyl with chlorine, bromine, and other substances, but without success. He also studied the action of zinc on ethyl iodide in the presence of water, and found that ethyl hydride was evolved. The results of this investigation were sent to the Chemical Society on June 17, 1849, and published in the Quart. Journ. Chem. Soc., 1850, **2**, 263—296, under the title "On the Isolation of the Organic Radicles." On March 15 and 16, 1849, the action of ethyl iodide on other metals was tried, and tin was found to be acted on with considerable ease. The results of all these experiments were included in the thesis for the Ph.D. degree, which was granted on June 30, 1849, Frankland being the first Englishman to graduate at Marburg.

Experiments were next made with zinc and methyl iodide, when zinc methyl was discovered with all its surprising properties. This compound and zinc ethyl were described in a paper on a new series of organic bodies containing metals and phosphorus (Quart. Journ. Chem. Soc., 1850, **2**, 297—299), and read on November 5, 1849.

In the autumn of 1849, Frankland went to Giessen and worked with Liebig until Christmas; here he experimented on the action of amyl iodide on zinc and obtained, in addition to amyl and zinc amyl, the compounds amyl hydride and amylene, which were previously unknown. This research was described at the Chemical Society on February 18, 1850, and published under the title "Researches on the Organic Radicles; Part II, Amyl" (Quart. Journ. Chem. Soc., 1851, **3**, 30—52). A section at the end of this paper refers to the constitution of alcohols, ethers, and the ammonia bases.

At Christmas, he went to Berlin with the intention of working in Rose's laboratory, but before the laboratory was opened he was offered the Professorship of Chemistry at Putney College in succession to Playfair and entered on his duties in the beginning of the year

1850. After organising the laboratory he tried the action of sunlight on ethyl iodide and found that, in the presence of mercury, mixtures of ethyl, ethyl hydride, and ethylene were formed. The paper on the action of solar light on ethyl iodide was read on November 4, 1850 (Quart. Journ. Chem. Soc., 1851, **3**, 322—347). The paper concludes with a discussion of the isomerism of methyl and ethyl hydrides and a reply to some criticisms by Hofmann. While at Putney the experiments on the ǎction of light on ethyl iodide in the presence of various metals were commenced and particular attention was paid to the effect produced by tin.

In January 1851, Frankland was appointed Professor of Chemistry at Owens College, Manchester, on its foundation, and immediately afterwards was married to Sophie Fick. The College was opened early in March, and a temporary laboratory was fitted up in a vacant house while the permanent laboratory and lecture-room were being built. These were completed and occupied in October 1851, and were, at that time, the most conveniently arranged in the country. The research on the action of metals on ethyl iodide in the presence of light was completed and the results brought before the Royal Society under the title "On a New Series of Organic Bodies containing Metals" on May 10, 1852 (*Phil. Trans.*, 1852, **142**, 417—444). In this paper are described the organo-tin compounds obtained from the stannethyl iodide, $SnEt_2I_2$, the product of the action of light on tin and ethyl iodide. This was believed to be a conjugate compound of tin and ethyl iodide, and as in these compounds the metal was supposed to retain its combining power unaltered, it was expected that the stannethyl iodide would combine with an additional quantity of a negative element. Cacodyl was at that time considered to be a conjugate compound, and, as it was capable of combining with chlorine and oxygen, the same property was looked for in the case of the tin compound and also of zinc methyl. The failure to effect these combinations threw new light on the combining powers of the elements, and this research was the starting point of the theory of atomicity or valency, which has had such an important influence on the progress of modern chemistry. The first of the organic compounds containing mercury, mercuric methiodide, was also described in this paper.

At Manchester, Frankland's attention was naturally drawn to technical chemistry, and he delivered a course of lectures on this subject at Owens College extending over two years. He also gave courses of lectures on Technological Chemistry at the Royal Institution in 1853 and 1857. In the *Memoirs of the Manchester Literary and Philosophical Society*, 2nd Series, **10**, 71—119 (January 13, 1852), he published a long paper, "Contributions to the Knowledge of the Manufacture of Gas," containing an investigation of White's hydro-

carbon process, which consisted in injecting water-gas into the retorts in which coal was being distilled.

During the investigations on the isolation of the organic radicles and the organo-metallic bodies, frequent analyses of gases were necessary, and this led to the publication in June 1853, in conjunction with Mr. W. J. Ward, of the paper on an improved apparatus for the analysis of gases (Quart. Journ. Chem. Soc., 1854, **6**, 197—205). This apparatus, which was an improvement on that of Regnault and Reiset, is the parent of many other forms of gas analysis apparatus which have since been devised.

The study of the manufacture of coal gas and its illuminating power gave rise to the invention of an improved gas burner, described in *Ure's Dictionary*, 7th edition, vol. **2**, p. 562. In this burner, the air supplied to the flame passes between the chimney and the surrounding globe before passing to the flame. In this manner both air and gas are heated before coming in contact, and the amount of light produced is increased 67 per cent. This burner was the precursor of those of Siemens, Grimston and Bower, and Wenham. A similar burner appears to have been devised as early as 1840, for Sir John Robison, in the *Edinburgh Philosophical Journal*, **28**, p. 299, states that such a burner was "proposed in Paris and much praised in London," but he says that it offers no advantage over a proper regulation of gas in an argand burner.

During the time that Frankland was at Manchester he published three more papers containing results of the researches on organo-metallic bodies. The first was on zinc ethyl, read February 9, 1855 (*Phil. Trans.*, 1855, **145**, 259—275); it contains a description of the iron digester in which sealed tubes were heated in water, so that the external pressure of the steam supported the walls of the tubes against the internal pressure of the contents; the copper digester for the preparation of zinc ethyl on a large scale is also described. The paper contains an account of the preparation and properties of zinc ethyl, and of the precautions necessary in manipulating this compound. The second research was "On a New Series of Organic Acids containing Nitrogen" (*Phil. Trans.*, 1857, **147**, 59—78; June 19, 1856). This deals with the action of nitric oxide on zinc ethyl and the products obtained from this reaction. And the third paper was on a new series of compounds derived from ammonia and its analogues, and published in the *Proc. Roy. Soc.*, 1856—1857, **8**, 502—506 (received June 18, 1857). This communication contains an account of the action of zinc ethyl on ammonia, aniline, diethylamine, oxamide, and acetamide, resulting in the replacement of hydrogen in these compounds by zinc.

On July 20, 1857, Frankland was appointed Lecturer on Chemistry

at St. Bartholomew's Hospital, and entered on his duties on October 1, in succession to Dr. Stenhouse, who had resigned in consequence of ill health. In 1859, he became Lecturer on Chemistry and Physics at Addiscombe, and on May 4, 1863, he succeeded Faraday as Fullerian Professor of Chemistry at the Royal Institution. He held these three appointments simultaneously during more than a year, for he retired from St. Bartholomew's on July 12, 1864, and shortly afterwards the Military College was abolished.

The work at St. Bartholomew's left more time for research than was available at Owens College, and the investigations of the organo-metallic bodies progressed, a note on sodium ethyl and potassium ethyl being published in 1858, and the Bakerian lecture entitled "Researches on Organo-metallic Bodies" being delivered at the Royal Society in 1859. Sodium and potassium ethyl were discovered by Mr. Wanklyn, and in the note above mentioned (*Proc. Roy. Soc.*, 1857—1859, **9**, 345—347) Frankland explains his failure to obtain these compounds by the action of sodium and potassium on ethyl iodide in his earlier experiments. Although action takes place between these substances, the products are merely metallic iodides and a mixture of ethylene and ethyl iodide. This was found to be due to the fact that sodium ethyl and ethyl iodide mutually decompose one another at the common temperature with formation of sodium iodide and a mixture of ethyl hydride and ethylene.

The Bakerian lecture (*Phil. Trans.*, 1860, **149**, 401) deals with further investigations on the tin, mercury, and zinc compounds. Pure stannic ethyl, $SnEt_4$, was obtained by the action of zinc ethyl on stannethyl iodide, $SnEt_2I_2$, and it was found to be incapable of further combination, showing that in this compound the combining powers of the tin are quite satisfied. Iodine, however, acts on it, replacing some of the ethyl by iodine. By the action of hydrochloric acid, stannic triethyl chloride, $SnEt_3Cl$, is formed with evolution of ethyl hydride. Stannic diethodi-iodide, by the action of zinc methyl, gave stannic diethodimethide, which, under the influence of iodine, gave distannic tetrethodi-iodide, $Sn_2Et_4I_2$, with separation of methyl iodide. Attempts were made to produce mercuric ethomethide by the action of zinc ethyl on mercuric methiodide, HgMeI, but without success, the products being mercuric ethide, zinc methyl, and zinc iodide. Mercuric methochloride, when acted on by zinc ethyl, gave a product the composition of which approached that of mercuric ethomethide, but by distillation it appeared to separate into mercuric ethide and mercuric methide. Attempts to produce zinc ethomethide were also unsuccessful. The preparation of pure zinc methyl on a large scale by the action of an ethereal solution of methyl iodide in the copper digester resulted in

the formation of a molecular compound of zinc methyl with ether, and when methyl ether was substituted for ethyl ether an analogous compound was produced.

While Frankland was at St. Bartholomew's, he became acquainted with Baldwin Francis Duppa, who had been a student of Hofmann's, and went to St. Bartholomew's to learn gas analysis. They soon became associated in original research, and the first paper they published appears to be a short one on boric ethide (*Proc. Roy. Soc.*, 1860, **10**, 568—570), presented to the Royal Society on July 7, 1860. The compound was prepared by the action of zinc ethyl on ethyl borate; this paper was merely a preliminary communication, the detailed description of these researches being published in 1862. On June 7, 1860, Frankland gave a lecture to the Chemical Society on organometallic bodies. It is published in the Journal, 1861, **13**, 177—235, and describes the work done up to that period.

About this time he undertook some experiments in physical chemistry. A short note dated November 7, 1861, was published in the *Phil. Mag.*, 1861, **22**, 472—473, on the blue band in the lithium spectrum, which had not been observed by Bunsen and Kirchhoff, and which he showed was due to increase of temperature.

On the 20th and 21st of August 1859, Frankland and Tyndall ascended Mont Blanc for the purpose of making scientific experiments. They made preparations for remaining a week upon the mountain, and started with a large party of 26 porters, to carry provisions and instruments, and 3 guides. On the night of the 20th they slept at the Grands Mulets, and on the 21st they slept in a tent about 12 feet below the summit of the ridge. Most of the porters having returned to Chamounix, the party, consisting of 11 persons, was the first to pass the night on the summit of Mont Blanc. On the following morning, Tyndall erected a post to which maximum and minimum thermometers were fixed, and also made some observations on solar radiation, while Frankland collected some air for analysis and also determined the rate of combustion of six stearin candles. He found that the loss of weight of each candle was 9·2 grams per hour, while at Chamounix he had found that 9·4 grams per hour were consumed, showing that the rate of combustion at the two different levels was practically the same. The party returned to Chamounix on the same day. The analysis of the air from Mont Blanc was described in a paper read to the Chemical Society on February 2, 1860, and published in the Journal, 1860, **13**, 22—30.

The experiments on the rate of combustion of candles on the summit of Mont Blanc led to a long experimental investigation on the influence of atmospheric pressure upon some of the phenomena of combustion, an account of which was read before the Royal Society on

June 20, 1861, and is printed in the *Phil. Trans.*, 1862, **151**, 629—653. It was not found practicable to determine experimentally the quantity of candle burnt in air at different pressures, for the observations were seriously interfered with by the heating of the enclosing apparatus; in the only experiment recorded, the quantity of stearin consumed in air at a pressure of 9 inches was more than 15 per cent. greater than that burnt at the ordinary pressure. It had been observed by Quartermaster Mitchell that time-fuses used at high altitudes burnt for a longer time than those used at sea level; experiments were tried by connecting a time-fuse to an iron tube in which the atmospheric pressure could be reduced, and the results fully confirmed those obtained by Mitchell, the rapid removal of the gases produced by the combustion of the gunpowder apparently cooling the next layer of the combustible and thus retarding the action. It was found that the rate of combustion of the fuse was reduced one-thirtieth for each diminution of one inch of the barometric pressure.

Experiments were tried on the amount of light produced by the combustion of candles in air of reduced pressure, but the results were not satisfactory owing to the irregularity of the combustion. An apparatus was constructed by means of which the light of a gas flame burning 0·65 cubic feet an hour could be compared with a similar flame burning the same quantity of gas in an enclosed space through which a current of air at reduced pressure was passing. The pressures varied from 6·6 inches to the ordinary barometric pressure, and it was found that the curve representing the amount of light produced is practically a straight line between 30 inches and 14 inches pressure, there being a diminution of approximately 5·1 per cent. of the luminosity at 30 inches for each reduction of 1 inch of pressure. Below 14 inches pressure, the diminution of light proceeds at a less rapid rate. Experiments were also made on the increase of luminosity on increasing the pressure. Difficulties were encountered at this stage, for all ordinary combustibles give smoky flames on a comparatively slight increase of pressure. A lamp containing amyl alcohol was used from the ordinary pressure to about 2 atmospheres; at a slightly higher pressure, the flame began to smoke. The increase of light obeyed approximately the same law as was found to represent the change of luminosity under reduced pressure. A lamp supplied with a mixture of five parts of common alcohol with one of amyl alcohol could be used up to a pressure of 4 atmospheres, but the luminosity increased much more quickly than calculated by the law.

On May 22, 1862, Frankland read a paper before the Royal Society on "A New Series of Organic Compounds containing Boron" (*Phil. Trans.*, 1863, **152**, 167—183). In this paper he recapitulates the work previously published in conjunction with Duppa and describes the preparation of

boric ethide, BEt_3, the action of hydrochloric acid on it with formation of boric diethochloride, BEt_2Cl, and the compound with ammonia, NH_3,BEt_3. Boric ethide by action of oxygen gives boric ethodiethylate, $BEt(EtO)_2$, which is decomposed by water into alcohol and boric ethodihydrate, $BEt(HO)_2$. He proves that the action of zinc ethyl on boric ether is not the simple removal of oxygen, as suggested by Kekulé, but is the replacement of the ethoxyl by ethyl, for, when boric ether is acted on by zinc methyl, the gaseous boric methide, BMe_3, is formed, the ethoxyl of the ether being replaced by methyl. Boric methide, like the ethide, forms a volatile compound with ammonia, and combines also with the hydrates of the alkali and alkaline earth metals.

On May 20, 1862, there appeared in the *Journal of Gas Lighting* a paper by Frankland "On the Igniting Point of Coal Gas," which was reprinted in the Journ. Chem. Soc., 1863, **1**, 398—403. He determined the inflaming point of the principal constituents of coal gas, and found that the vapour of carbon disulphide inflames at about 150°, hydrogen at the temperature of an iron rod heated to redness in daylight, carbonic oxide at a higher temperature, marsh gas and olefiant gas at still higher temperatures. A mixture of carbonic oxide with 3 per cent. of carbon disulphide vapour inflamed at about 175°, and a mixture of hydrogen and 3 per cent. of carbon disulphide vapour at 215°. The inflaming point of olefiant gas was not lowered by admixture of carbon disulphide, and the presence of a small quantity of olefiant gas very much raised the inflaming points of mixtures of carbonic oxide with carbon disulphide vapour and of hydrogen with the same vapour. Marsh gas was not inflamed by sparks from flint and steel, although such sparks easily inflame hydrogen and coal gas. He points out that Davy lamps must be used very cautiously in mixtures of air and coal gas.

About this time, Frankland's attention was occupied by the synthesis of organic compounds by the use of zinc ethyl, and on January 15, 1863, a paper was read before the Royal Society on the synthesis of leucic acid (*Proc. Roy. Soc.*, 1862—1863, **12**, 396—398). When zinc ethyl and ethyl oxalate are mixed, an energetic action takes place; if the product is mixed with water and distilled, a liquid passes over of the same composition as that of the ethyl salt of leucic acid, an acid obtained by Strecker by the action of nitrous acid on leucin. The ethereal salt is the result of replacing one atom of oxygen in ethyl oxalate by two semi-molecules of ethyl, and was called ethyl diethoxalate. In conjunction with Duppa, Frankland afterwards found that leucic acid is isomeric, but not identical, with diethoxalic acid. This was the first member of the lactic series which was obtained artificially, and its discovery led to a series of investigations by Frankland and Duppa on the acids of the

lactic and acrylic series. In a series of notes presented to the Royal Society, the authors recorded the progress of their work. These papers were entitled "Notes of Researches on the Acids of the Lactic Series." No. 1 is "On the Action of Zinc upon a Mixture of Iodide and Oxalate of Methyl" (*Proc. Roy. Soc.*, 1864, **13**, 140—142). No. 2, "Action of Zinc upon a Mixture of Iodide of Ethyl and Oxalate of Methyl" [1864] (*Proc. Roy. Soc.*, 1865, **14**, 17—19). No. 3, "Action of Zinc Ethyl on Ethylic Leucate" (*Proc. Roy. Soc.*, 1865, **14**, 79—83). No. 4, "Action of Zinc upon Oxalic Ether and the Iodides of Methyl and Ethyl mixed in Atomic Proportions" (*Proc. Roy. Soc.*, 1865, **14**, 83—86). No. 5, "Action of Zinc upon a Mixture of Ethyl Oxalate and Amyl Iodide" (*Proc. Roy. Soc.*, 1865, **14**, 191—198). These papers were read between February 18, 1864, and April 27, 1865.

On June 15, 1865, the authors read a paper at the Chemical Society entitled "Transformation of the Lactic into the Acrylic Series of Acids" (Journ. Chem. Soc., 1865, **13**, 133—156), in which they showed that the ethereal salts of the acids of the lactic series, which they had produced by synthesis, were transformed by the action of phosphorous chloride into ethereal salts of acids of the acrylic series, and that the acids of the acrylic series obtained from these esters when heated with caustic potash gave two acids of the acetic series. From the results obtained, the constitution of the acids of the acrylic or oleic series obtained artificially, and that of some of the natural oleic acids, was determined.

The joint authors read a paper before the Royal Society on April 27, 1865, "Notes of Synthetical Researches on Ethers. No. 1. Synthesis of Butyric and Caproic Ethers from Acetic Ether" (*Proc. Roy. Soc.*, 1865, **14**, 198—204), and on July 13 they forwarded another paper, which was read on November 16, 1865, "Synthetical Researches upon Ethers. 1. Synthesis of Ethers from Acetic Ether" (*Proc. Roy. Soc.*, 1865, **14**, 458—464, and *Phil. Trans.*, 1866, **156**, 37—72). In these papers, they describe the results of the consecutive action of sodium and ethyl and methyl iodides on ethyl acetate, by which they obtained butyric and caproic ethers, sodic and disodic acetic ethers, the carboketonic ethers, and the ketones prepared from them. This paper concludes with theoretical considerations on the constitution and chemical relations of the ethereal salts and ketones derived from the duplication of the molecule of ethyl acetate, and on the constitution of the fatty acids, in which it is shown that the fatty acids may be regarded as containing the negative group CO(OH) united to a positive radicle, either hydrogen or methyl, or methyl with one or more atoms of the hydrogen replaced by other positive groups. It is also pointed out for the first time how numerous are the isomeric modifications of the fatty acids which are possible by varying the constitution of the positive radicle.

In August 1865, Frankland had intended accompanying his brother-in-law, Professor Fick, and Professor Wislicenus in their expedition to the Faulhorn, where they intended to institute some experiments on the origin of muscular power. The weather was unpropitious and Frankland had to leave Geneva, where he was waiting for his colleagues; they, however, carried out the experiments a fortnight later in his absence. The method adopted was to climb the mountain after having abstained for about 18 hours from albuminoid food, and by the determination of the amount of urea excreted they hoped to obtain evidence that the work performed resulted from the oxidation of muscle. It was found, however, that the measured work far exceeded that which could have been performed by the oxidation of the muscle and that the energy must therefore have been partly supplied by the non-nitrogenous food that they had consumed.

Frankland undertook to determine the amount of heat produced by the combustion of various food materials and the experiments were carried out by means of Lewis Thompson's calorimeter, the organic substances being burnt under water by means of a mixture of potassium chlorate and potassium nitrate. From the quantity of energy produced by the combustion of the food, it was shown that the source of the muscular power was not the muscle that was wasted, but the carbon and hydrogen of the food that was oxidised in the body, and thus served as fuel, the muscle acting merely as the machine which rendered the energy available. The results of this research were published in a paper in the *Philosophical Magazine*, 1866, **32**, 182—199. Frankland also gave a lecture on the subject at the Royal Institution on Friday evening, June 8, 1866.

Meanwhile the organo-metallic bodies were not neglected, for on November 19, 1863, Frankland and Duppa read a paper before the Chemical Society "On a New Method of producing the Mercury Compounds of the Alcohol Radicles" (Journ. Chem. Soc., 1863, **1**, 415—425), in which they showed that when the iodides of methyl, ethyl, and amyl, mixed with a small quantity of ethyl acetate, are brought into contact with sodium amalgam at the ordinary temperature, the corresponding mercury compounds are formed; and on December 3, 1863, another paper was read at the Chemical Society "On a New Reaction for the Production of the Zinc Compounds of the Alcohol Radicles" (Journ. Chem. Soc., 1864, **2**, 29—36), describing the action of zinc on mercuric methide, ethide, and amylide, by which the zinc methyl, zinc ethyl, and zinc amyl were readily obtained in a state of purity.

On February 14, 1866, the authors sent to the Royal Society a paper on "Researches on Acids of the Lactic Series. No. 1. Synthesis of Acids of the Lactic Series," which was read on March 1, 1866 (*Proc. Roy.*

Soc., 1867, **15**, 25—28; *Phil. Trans.*, 1866, **156**, 309—360). This paper includes the results of the five notes read between February 18, 1864, and April 27, 1865, entering more fully into the subject and giving analyses of the products. In the theoretical considerations which conclude this paper, they propose the name of oxatyl for the compound radicle CO(OH), it being the radicle of which oxalic acid is the isolated molecule. They show that this radicle exists in almost all organic acids and that it is to this radicle that these compounds owe their acidity, hence the expression "An organic acid containing *n*-semimolecules of oxatyl is *n*-basic." Thus, they consider lactic acid to be a monobasic acid, a matter which had been previously much contested. They divide the lactic acids into eight classes and explain the reasons for this classification. In a note they advise chemists to use Crum Brown's graphic formulæ, a recommendation which has been almost universally followed, and by means of such formulæ they explain the isomerism in the lactic series. They also deal with the proximate analysis of the acids of the lactic series by which they ascertain the presence of the various radicles in the acids.

In September 1866, Frankland communicated to the Chemical Society "Contributions to the Notation of Organic and Inorganic Compounds" (Journ. Chem. Soc., 1866, **4**, 372—395). The study of organic compounds and the elucidation of their constitution by means of graphic formulæ led him to devise a system of symbolic notation which would represent the same ideas as were conveyed by the graphic formulæ. By employing symbols to represent compound radicles, as Ho for (OH), Ko for (OK), Bao″ for (O_2Ba), Me for (CH_3), &c., and constructing the formula of a compound by placing the symbol of the binding or grouping element (printed in thick type) before the symbols of the elements and compound radicles to which it is combined, and by using a bracket to show that the elements whose symbols are next to the bracket are directly combined, it is possible to represent the constitution of compounds whether inorganic or organic.

Thus, ammonic chloride and nitrate are represented by NH_4Cl, NO_2Amo. Sulphuric acid, the sulphates of potassium and barium by SO_2Ho_2, SO_2Ko_2, SO_2Bao''. Ferric sulphate by $S_3O_6Fe_2o^{vi}$. Alcohol and acetic acid by $\begin{cases} CH_3 \\ CH_2Ho \end{cases}$, $\begin{cases} CH_3 \\ COHo \end{cases}$. Lactic acid by $\begin{cases} CMeHHo \\ COHo \end{cases}$, and tartaric acid by $\begin{cases} CO\,Ho \\ CHHo \\ CHHo \\ CO\,Ho \end{cases}$, &c. It is obvious that these formulæ can be at once transformed into graphic formulæ if required.

On January 17, 1867, Frankland and Duppa read a paper before the Chemical Society on "Synthetical Researches on Ethers. No. 2.

Action of Sodium and Isopropyl Iodide upon Ethylic Acetate" (Journ. Chem. Soc., 1867, 5, 102—116). The results of this action were found to be quite analogous to those obtained with the other iodides.

During the time that Frankland was at the Royal Institution, he was engaged in professional work which brought him in contact with many problems of an economic nature. Thus, in 1859, when the condition of the Thames in London became very offensive, he and Dr. Hofmann were requested by the Metropolitan Board of Works to examine various proposals which had been made for the deodorisation of sewage, and when, in 1865, he succeeded Dr. A. W. Hofmann as Professor of Chemistry at the Royal School of Mines, he continued the reports on the monthly analyses of the metropolitan waters which had been commenced a short time previously at the Royal College of Chemistry. He became much interested in the water supply of towns and he read a paper before the Chemical Society on March 15, 1866, on "The Water Supply of the Metropolis during the Year 1865—1866" (Journ. Chem. Soc., 1866, 4, 239—248). This led him to investigate the methods in use for the analysis of water, and on January 16, 1868, he delivered a lecture before the Chemical Society "On the Analysis of Potable Waters" (Journ. Chem. Soc., 1868, 6, 77—108). In this lecture, the investigations on water analysis, made in conjunction with Dr. H. E. Armstrong, are fully dealt with, and descriptions are given of the processes which they suggest for a more trustworthy analysis of waters. The organic carbon and nitrogen are determined by combustion of the solid residue from the water with lead chromate and oxide of copper, the combustion being carried out in a tube previously exhausted by a Sprengel pump, and from which the resulting carbon dioxide and nitrogen are removed by the same pump and the gases measured. The manipulations necessary for this process and for the determination of nitrogen in the state of ammonia and of nitrates and nitrites are given in detail and the objections to other methods are stated. This paper was succeeded by another "On a Simple Apparatus for determining the Gases Incident to Water Analysis" (Journ. Chem. Soc., 1868, 6, 109—120). This is a simplification of the gas analysis apparatus previously described in 1853.

In 1868, Frankland was appointed a member of the Royal Commission to inquire into the Best Means of preventing the Pollution of Rivers. A laboratory was fitted up in Victoria Street, Westminster, in which a large amount of experimental work was carried on under the supervision of the late Mr. W. Thorp. The work was continued until 1874, and six voluminous reports were issued by the Commission during this period.

In March 1867, Frankland gave, at the Royal Institution, a course of lectures on coal gas, in which he stated that some experiments had

led him to doubt the correctness of Sir Humphry Davy's theory that the light of gas and candle flames is due to the incandescence of solid particles in the flames, and in a paper read before the Royal Society on June 11, 1868, "On the Combustion of Hydrogen and Carbonic Oxide in Oxygen under Great Pressure" (*Proc. Roy. Soc.*, 1868, **16**, 419—422), he shows that there are many luminous flames which cannot possibly contain solid matter, such as those produced by the combustion of arsenic and phosphorus in oxygen, the temperature produced by the combustion being more than sufficient to retain the products of combustion in the gaseous condition. He attributes the luminosity to the incandescence of the dense vapours present in the flame. A jet of hydrogen one inch long gives very little light when burnt in oxygen at the ordinary pressure, but when the pressure is raised to 10 atmospheres a white flame is produced, which is sufficiently bright to enable one to read a newspaper at the distance of two feet from the flame, and the spectrum of the flame is continuous from red to violet. The spectrum of carbonic oxide burning in oxygen at a pressure of fourteen atmospheres is very brilliant and quite continuous. When sparks from an induction coil are passed through hydrogen, oxygen, chlorine, and sulphurous anhydride, the brilliancy of the sparks increases with increase of density of the gas. On June 12, 1868, a lecture was given on this subject at the Royal Institution (*Proc. Roy. Inst.*, 1869, **6**, 419—423).

About 1868, Mr. J. Norman Lockyer was working at the Royal College of Chemistry, and three short papers were published by the joint authors in 1869. The first was read at the Royal Society on February 11, 1869, "Preliminary Note of Researches on Gaseous Spectra in relation to the Physical Constitution of the Sun" (*Proc. Roy. Soc.*, 1869, **17**, 288—291). They found that the line seen near *D* in the spectrum of the chromosphere, afterwards known as the helium line, was not due to hydrogen, that the widening of the green line *F* at the lower portion of the chromosphere was due to increase of pressure, and that the gas at the upper portion of the chromosphere must be in a state of excessive tenuity. They also suggest that the photosphere of the sun does not consist of solid or liquid matter, but of gas of sufficient density and temperature to produce a continuous spectrum. The second note was read on June 10, 1869, "Researches on Gaseous Spectra in relation to the Physical Condition of the Sun, Stars, and Nebulæ. Second Note" (*Proc. Roy. Soc.*, 1869, **17**, 453—454), and deals principally with the spectra of hydrogen and nitrogen, which are each reduced to single lines in the green when the temperature is reduced. The third note, with the same title, was communicated on July 14, 1869 (*Proc. Roy. Soc.*, 1870, **18**, 79—80); it deals principally with the spectrum of magnesium, some of the lines in which are

shorter than others, both when magnesium is projected into the chromosphere and when sparks are produced between poles of magnesium.

On February 2, 1871, Frankland read a paper before the Chemical Society on "The Development of Fungi in Potable Waters" (Journ. Chem. Soc., 1871, **9**, 66—76). This refers to the test for purity of potable water suggested in the previous year by Mr. Heisch, which consisted in dissolving in the water a small quantity of pure sugar and keeping the solution for some days in a warm place: if the water was contaminated, a fungus was found to be produced. Frankland tried many experiments with this test, and found that the presence of a phosphate was necessary for the growth of the fungus, whatever the source from which the water was obtained.

On February 17, 1876, another lecture was delivered at the Chemical Society "On Some Points in the Analysis of Potable Waters" (Journ. Chem. Soc., 1876, i, 825—851), giving the results of eight years' experience of the methods described in 1868, together with further details of manipulation. The term "previous sewage contamination," which had been adversely criticised, was defended. The variations in the condition of the London waters are shown by diagrams, and objections are raised to other methods of water analysis in vogue at that period.

In 1876, Frankland returned to the study of the organo-boron compounds, and on June 15 he read before the Royal Society a paper on organo-boron compounds (*Proc. Roy. Soc.*, 1877, **25**, 165—168). He gave another method of preparing boric ethide by passing the vapour of boric chloride into zinc ethyl. By the action of two molecules of boric ethylate on one of zinc ethyl, he obtained diboric ethopenthylate, a liquid boiling at about 112° and distilling unchanged. This has the composition of a compound of boric ethylate with boric etho-diethylate, and it appears to dissociate into these compounds when volatilised, for the vapour density is only one-half of the theoretical. It probably contains two atoms of pentad boron united together by two bonds of each, forming a hexad group, with which one semi-molecule of ethyl and five of ethoxyl are combined. Ammonia-boric methide, previously discovered, may have a similar constitution, the pentad nitrogen and boron being united by two bonds of each, and the hexad group combined with three atoms of hydrogen and three semimolecules of methyl. Boric diethethylate, boric diethohydrate, and boric ethethylate-hydrate are also described in this paper.

The foregoing account by no means includes all the papers that Frankland published, but it contains the most important, almost all of them containing discoveries which have had a great influence on the progress of science; many of the remaining papers are continuations of the work done in earlier years.

Frankland was an excellent manipulator; his early researches required such careful experiment, and were, of course, carried out without the help of others, that he acquired great facility in manipulation. Even after circumstances had placed at his disposal the assistance of students and other co-workers, he still continued to do a large amount of work with his own hands. He took great care in experimentally illustrating his lectures and devised a large number of striking experiments, many of which are still used by lecturers, but their origin has been forgotten. His retiring character was so marked that even those who were in frequent contact with him heard very little from his lips of what he had previously accomplished, and it was only from his published work that they learnt the extent of his early successes. He was always kind, considerate, and helpful to his students and assistants.

Sir Edward Frankland in his autobiography tells us that in his youngest days he was very fond of books of travel, but that he had not any opportunity of going beyond a short distance from home until, at the age of 17, he spent a week in Cumberland and Westmoreland. In 1845 he came from Lancaster to London, in 1847 he went to Marburg, crossing from Dover to Ostend, and by the Rhine to Mayence, and on to Frankfort and Marburg. Tyndall and he went to Paris to spend their summer vacation in 1848, and he was there during the revolution at the end of June, living in one of the most disturbed districts. In October 1848 he again went to Marburg, and the next year to Giessen, and in the beginning of 1850 he was for a short time in Berlin. After his marriage he went to Cassel in 1852, and in 1855 he took a cottage at Windermere, where he and his family resided during the vacations; here he had a small yacht, and later he kept a yacht at Cowes. His mountaineering in Switzerland gave rise, as we have seen, to investigations on combustion under different pressures, as well as to papers and lectures on the glacial epoch, thermometric observations, and experiments on solar radiation. In 1863 he paid his first visit to Norway, to which country he became much attached and where he died. He also went to Spain and Algiers. He attended the meeting of the British Association at Montreal in 1884, and afterwards went to the Yellowstone Park and Chicago. In 1886 he went to the Riviera, Naples, Vesuvius, and Capri. He was in Berlin in 1890. This very meagre account of his travels will, however, show that his early predilections for travel were continued during his whole life.

While living at Haverstock Hill, between 1857 and 1870, Frankland took a great interest in gardening: he also at that time ground and silvered a 7-inch glass speculum and fitted it in a telescope, which he used for astronomical purposes, making drawings of the moon and

planets. From 1870 to 1880 he resided in Lancaster Gate, and in the latter year he moved to the Yews, Reigate. Here he had a fine observatory. He lighted the house by electricity, supervising the working and making some of the fittings himself. This led to his investigations of the action of secondary batteries, described in a paper sent to the Royal Society on February 21, 1883, entitled "Contributions to the Chemistry of Storage Batteries" (*Proc. Roy. Soc.*, 1883, **35**, 67—70). He also took much interest in his gardens and hot-houses.

Frankland was elected a Fellow of the Chemical Society on December 20, 1847. He served on the Council in 1850—1851 and again in 1858—1859; he was Foreign Secretary from 1861—1868, Vice-President in 1860, 1868, and 1870, and President from 1871—1873. By a curious oversight, his connection with the Chemical Society is not mentioned on the title page of his collected papers, entitled "Experimental Researches in Pure, Applied and Physical Chemistry," published in 1887. He was one of the founders and the first President of the Institute of Chemistry from 1877 to 1880, and afterwards a Vice-President and Censor. He was elected Fellow of the Royal Society on June 2, 1853, and served on the Council in 1857—1859; 1865—1867; 1875—1877, and 1886—1888. He was Foreign Secretary from 1895 until his death. He was awarded a Royal Medal in 1857 and the Copley Medal in 1894. He was also a member of many of the foreign learned societies and academies. He received the honorary degree of D.C.L. of Oxford in 1870, and the LL.D. of Edinburgh in 1884. On the occasion of the Diamond Jubilee of Queen Victoria in 1897 he was created K.C.B.

Frankland was twice married, first to Fräulein Sophie Fick, on February 27, 1851, who died at Davos on January 7, 1874. His second wife was Miss Ellen Frances Grenside, whom he married on May 11, 1875. She died in January, 1899, after a long illness.

He left two sons and two daughters by his first wife, and two daughters by his second. His elder son is a remarkable mathematician, the younger is the well-known Professor of Chemistry at the University of Birmingham. Of recent years, Sir Edward Frankland went almost annually to Norway, where he spent much of his time in fishing, although during the last few years of his life he devoted his time spent in his cottage at Golaa in Gudbrandsdalen to literary work. He died there, after ten days' illness, on August 9, 1899.

HERBERT MCLEOD.

JOHN HALL GLADSTONE.

BORN MARCH 7TH, 1827; DIED OCTOBER 6TH, 1902.

FOR many generations the ancestors of John Hall Gladstone lived in the town of Kelso in Roxburghshire, where they carried on the business of damask weavers. But in the early part of the nineteenth century the cottage hand-loom was being superseded, and John Gladstone was driven to seek his fortune in London. Here in February 1816 he entered the drapery establishment of Mr. Cook, in Cheapside, in the humble position of shop-boy; but he soon rose to be traveller and buyer, and in 1824 was taken into partnership. He then married a young cousin, Alison Hall, whose father had a drapery business in Bishopsgate Street, and in due time three sons were born to them. John Hall, the eldest, was born at 7, Chatham Place West, Hackney, and was baptised at Albion (Presbyterian) Chapel, Moorfields. The three brothers were educated entirely at home under tutors, and from very early days all showed a strong inclination toward natural science. In 1842 the father, John Gladstone, retired from business, and soon afterwards the family spent upwards of a year in travelling on the Continent. Part of this time was passed in Italy with their old friends Mr. and Mrs. Tilt and their daughter May, who in 1852 became the eldest son's wife.

From early years John Hall Gladstone had shown strong religious tendencies, and when, at the age of seventeen, the question of his future career came to be discussed, he wished to enter the Christian ministry. From this course he was dissuaded both by his father and by Mr. Tilt, and in December 1844 he entered University College as a student. Here he attended Graham's lectures on chemistry and worked in his private laboratory, and here he prepared his earliest contributions to scientific literature. His first paper, containing an "Analysis of Sand from St. Michael's Bay, Normandy," was read at a meeting of the Chemical Society on November 16, 1846, when he was but nineteen years of age. On June 7 in the following year a more important communication, on "Gun Cotton and Xyloidine," showed that, although so young, he possessed the qualifications necessary for serious scientific investigation, and a gold medal for original research was awarded him by the College. Later in the same year he went to Giessen to work under Liebig, returning in April 1848 with the degree of Doctor of Philosophy. The subject of his dissertation can only be conjectured, but it is probable that the paper on the "Artificial Formation of Urea from Fulminic Acid" (Quart. Journ. Chem. Soc., 1, 228), which appears in Liebig's *Annalen* for 1848, contains the results of the work under-

taken with a view to graduation. But although Gladstone had thus formally adopted the pursuit of science as his career, he continued throughout his life to take an active part in religious work. In Clapham his parents were members of the Rev. James Hill's Congregational Church, and here he taught in the Sunday School, beside conducting services in a Mission Room at White Square. Later on he held a Bible Class for young men on Sunday afternoons, and until the end of his life he was intimately connected with the work of the Young Men's Christian Association. For many years he was the chief organiser of the Sunday afternoon devotional meeting held annually at the meeting of the British Association. In 1850 he was appointed Lecturer in Chemistry to St. Thomas's Hospital, a post which he held for two years, and in 1853, at the age of 26, he was elected into the Royal Society. After the death of his father-in-law in 1861 there was no necessity for Dr. Gladstone to earn money; but he was now so well known, both as a scientific man and a philanthropist, that he had no difficulty in filling his days with useful work. In 1864 he had the deep misfortune to lose his wife and their eldest daughter and only son. This, however, seems to have been followed by only temporary suspense of activity, social and scientific.

In 1863–4 and again in 1866–8 he served on the Council of the Royal Society, and having been a member of the Royal Commission on Lighthouses, Buoys, and Beacons from 1859 to 1862, he became a member of the Gun Cotton Committee in 1864–8.

In politics Gladstone was a Liberal, and on more than one occasion he was tempted to enter Parliament. In 1868 he unsuccessfully contested the borough of York. In 1869 he married Margaret, daughter of the late Rev. Dr. David King, and niece of Lord Kelvin. This lady died in 1870, leaving one daughter.

From 1874–7, Gladstone held the Fullerian Professorship of Chemistry at the Royal Institution, and was first President of the Physical Society, of which he was one of the founders. He was President of the Chemical Society from 1877–9, and in 1898 he was one of the six past Presidents of that Society who had been Fellows for upwards of fifty years, and in whose honour a banquet was given under the chairmanship of the President, Professor Dewar.

Gladstone will be long remembered for his services to education, especially in connection with the introduction of the rudiments of science into the curriculum of Elementary Schools. From 1873 to 1894 he was a member of the London School Board, for three years he was Vice-Chairman of the Board, and for many years he was Chairman of the Books and Apparatus Sub-Committee. He was also for several years, and up to the time of his death, an Almoner of Christ's Hospital, and took much interest in the arrange-

ments for the improved teaching of experimental science in the new buildings at Horsham. Dr. Gladstone was an expert phonographer, having learned the art so early as 1846, and he made use of it for note-taking as a student and for general purposes of composition throughout his life. This led him when a member of the School Board to institute inquiries into the methods of teaching reading, and as a result he came to the conclusion that a reform in English spelling was very desirable. He was successful in 1876 in inducing the School Board to pass by a large majority a resolution in favour of a change, a memorial was subsequently presented to the Committee of Council on Education, and in 1879 the Spelling Reform Association was constituted. Although phonetic spelling was not adopted, much good was accomplished in the abolition of the old-fashioned spelling-books, and to Dr. Gladstone's efforts in urging the importance of shorthand is mainly due the teaching of this art which has been so widely adopted.

Dr. Gladstone was very fond of London, and although from childhood he had taken much interest in natural history, and although he often praised the country, not unfrequently in verse, he seems never to have wished to live out of the metropolis. It only remains to be mentioned that he spoke French readily, and frequently attended the summer meetings of the Association Française pour l'Avancement des Sciences, and was also at one or two meetings of the Swiss Association.

In recognition of his services to education he was elected an Honorary Fellow of the College of Preceptors. He also received the degree Sc.D. at the celebration of the Tercentenary of Trinity College, Dublin, in 1892, and the Davy Medal from the Royal Society in 1897.

In 1880 he became a member of the Company of Wheelwrights, and as a liveryman took part in the last year of his life in the election of the Lord Mayor, at the Guildhall, on Michaelmas Day. On the day of his death, October 6, 1902, he presided in the afternoon at a meeting of the Christian Evidence Society, and, after walking part of the way home, he went into his study, and was found lifeless there as the result of failure of the heart. He was buried the following Friday in Kensal Green Cemetery.

As an investigator in pure chemistry and in physical chemistry Gladstone accomplished a prodigious amount of work. Beside 140 papers standing under his own name alone, there are no fewer than 78 written in collaboration with other workers, as follows: with Sir David Brewster 1, with Rev. T. P. Dale 5, with George Gladstone 7, with J. D. Holmes 2, with Alfred Tribe 41, with Walter Hibbert 20, and with Dr. W. H. Perkin 2. This fertility is partly explained in his speech at the banquet in 1898, for having ample means at his command he was always able to keep in his laboratory a trained

assistant whose work could proceed in his absence. He was a scientific amateur in the best sense of the word.

Some of the subjects in what may be called pure chemistry to which Gladstone's attention was in his early years directed have already been mentioned. Others which deserve notice were the production and properties of phosphamide and similar compounds, begun at Liebig's suggestion and revised ten years later; an inquiry into the composition of the so-called iodide of nitrogen (1852), in which the author's results seemed to justify the adoption of the formula previously given to the compound by Bineau, viz. NHI_2. Not only had this subject been previously much investigated with results which were not concordant, but from that time onward the question remained unsettled until 1899, when the formula $N_2H_3I_3$, which had been proposed by Bunsen half a century before, was established by Chattaway.

A more important inquiry is embodied in the paper, which appears in the *Philosophical Transactions* for 1855, on "Circumstances modifying the Action of Chemical Affinity." Here, after giving the history of ideas relating to chemical affinity from Bergman down to Berthollet and onwards, the author proceeds to examine the question, arising out of the researches of Bunsen and Debus, whether when two substances act on each other an increase in the quantity of one of them leads to a corresponding increase in the amount of chemical change observed, and whether such change occurs continuously, or *per saltum*, in atomic proportions. In the work of Bunsen on the products of the explosion of carbonic oxide and hydrogen with various proportions of oxygen the resultant carbon dioxide and water are incapable of acting on each other, and in Debus's experiments on the precipitation of mixed barium and calcium chlorides by a carbonate the precipitated earthy carbonates are removed from the reach of further chemical action. In Gladstone's experiments, on the other hand, the products of the interchange as well as the unaltered residue of the original materials remain in the field.

The most interesting results were obtained by observation of the changes of colour which occur in the formation of the red ferric thiocyanate by bringing together in aqueous solution various ferric salts and an alkaline thiocyanate in different proportions. The principal conclusions arrived at are briefly as follows:—

When two or more binary compounds are mixed under such circumstances that all the products are free to act and react, each positive element combines with each negative element in constant proportions, which are independent of the manner in which the elements were originally combined and which are not merely the resultant of the action of the various affinities concerned, but are dependent also on the mass of each of the substances in the mixture.

An alteration in the mass of any one of the binary compounds present alters the amount of every one of the other binary compounds, and that in a regularly progressive ratio, sudden transitions only occurring where a substance is present which is capable of combining with another in more than one proportion. The theory of Berthollet is thus confirmed. The phenomena which present themselves when precipitation, volatilisation, or crystallisation occurs are different because one of the substances is removed from the field of action. Hence there is a fundamental error in all conclusions as to what compounds exist in a solution, drawn from such empirical rules as that "the strongest base combines with the strongest acid." This paper was justly considered so important that it was reprinted in full in the Quarterly Journal of the Chemical Society, vol. 9. The same volume contains another paper directly contributed to the Chemical Society, entitled "Some Experiments illustrative of the Reciprocal Decomposition of Salts," which is devoted to a discussion of some apparent exceptions to the law quoted above and disposes of them all. A further contribution to the same subject occurs in vol. 11, on the "Chemical Action of Water on Soluble Salts." The concluding sentence, which declares that "the actual state of a dissolved salt is beyond the expression of any of our formulæ," is not far from a true representation of the state of knowledge on this subject at the present time.

There is no doubt, however, that optical phenomena and the properties of elements and compounds in relation to light formed the subjects which possessed the greatest fascination for Gladstone. This comes out quite early in his career, and in a variety of forms. Thus in 1854 he lectured at the Royal Institution on "Chromatic Phenomena exhibited by Transmitted Light." In 1855 there were "Notes on some substances which exhibit the Phenomena of Fluorescence," in the *Edinburgh New Philosophical Journal*, and in 1856 on "Some Dichromatic Phenomena among Solutions," at the meeting of the British Association. In 1858 he drew attention to the use of the prism in qualitative analysis (Quart. Journ. Chem. Soc., 10, 79), and discovered the remarkable lines in the absorption spectrum of didymium, a substance long afterwards resolved by Auer von Welsbach into the two elements known as praseo- and neo-dymium. A little later he studied the absorption spectrum of the atmosphere, and found that the lines of Fraunhofer varied according to the time of day, and that the change must be due to some constituents of the earth's atmosphere. In this research he was joined by Sir David Brewster, and together they produced a paper on the lines of the solar spectrum which appears in the *Phil. Trans.*, for 1860.

But the most important work of Gladstone's in this direction was undoubtedly the long series of observations on the refraction and

dispersion of liquids. This apparently originated with a study of the "Influence of Temperature on the Refraction of Light," undertaken in concert with the Rev. T. P. Dale (*Phil. Trans.*, 1858). This was followed by the important "Researches on the Refraction, Dispersion, and Sensitiveness of Liquids," in the *Phil. Trans.* for 1863.

Representing the refractive index by μ, the expression $\mu - 1$ is termed by the authors the refractive energy of the substance, and this multiplied by the volume or divided by the density, d, gives the specific refractive energy, $\frac{\mu - 1}{d}$. The refractive power of liquids is, like some other physical properties, additive in character, and every liquid has a specific refractive energy composed of the specific refractive energies of its component elements more or less modified by the manner of combination. The specific refractive energy being almost independent of temperature, solution, or even chemical combination, the product of this value multiplied by the molecular weight gives the molecular refractive energy from which refraction equivalents for the elements may be deduced. These refraction equivalents calculated from the refractive energy of different compounds come out nearly but not quite identical, the mean value for potassium, for example, derived from observations on the chloride, cyanide, thiocyanate, and hydroxide is 8·2, while the ethylate, formate, acetate, and tartrate give a mean value 7·8. With such constants the molecular refractive powers of compounds can be calculated, and are generally found to agree very well with those deduced from direct observation of the same compounds. In some cases, carbon and nitrogen for example, the element exhibits more than one atomic refraction, which appears to be connected with its mode of combination. This part of the subject has been pursued for many years by Professor J. W. Brühl, but to Gladstone's laborious observations we owe practically all our knowledge of refractive equivalents.

Another memorable series of researches commenced about 1872, in conjunction with his assistant Alfred Tribe, resulted in the discovery of the copper-zinc couple, and its application to the production of the organo-zinc compounds and to other purposes. The couple has long since found its way into every laboratory in the world, and as a reducing agent has met with applications not only in connection with carbon compounds but for many purposes in analysis.

Notwithstanding or perhaps in consequence of Gladstone's activity as an experimenter, an occupation which almost necessarily leads to the writing of many papers, he did not produce many books. In 1872 he brought out a Biography of Faraday, with whom he had been on terms of close friendship. In 1883 a series of papers on the "Chemistry of the Secondary Batteries of Planté and Faure" were collected into a



little volume published by Macmillan. A small work on "Spelling Reform from an Educational Point of View" was also published by Macmillan in 1878. It will readily be understood from what has already been stated that a large number of pamphlets, papers, and magazine articles on social, educational, and religious subjects also came from his pen.

Personally Gladstone was one of the most kindly and genial of men, with an old-fashioned but never-failing courtesy of manner. It was characteristic of him that when called upon to speak, even in a scientific meeting, he almost invariably addressed his audience as "Friends!" Eager in the pursuit of knowledge and anxious for its diffusion, he divided the long years of an active and useful life between the search after truth and the promotion of the social, moral, and intellectual improvement of his fellow-men. His memory is secure in the respectful admiration of his contemporaries, and by future generations his name will be remembered as one of those who helped to lay the foundations of modern physical chemistry.

W. A. Tilden.

WLADIMIR WASSILJEWITSCH MARKOWNIKOFF.

Born December 22nd, 1838; Died February 11th, 1904.

Wladimir Wassiljewitsch Markownikoff was born on December 22 (N.S.), 1838, in the neighbourhood of Nischnij Nowgorod. Here he attended the preparatory school; and, after passing through the "Gymnasium," entered in 1856 the University of Kazan as a "Cameralia" student. In this university he took his doctor's degree in 1861. About this time he first came in contact with the striking personality of Butlerow, who attracted him strongly; and who, having recently returned from Germany and France charged to the full with the new doctrines of molecular structure, was lecturing and demonstrating enthusiastically on these subjects. In 1862, having completed his course of study, he was appointed Assistant in the department of Inorganic Chemistry. He married in the following year.

In 1865, Markownikoff was sent abroad by the Russian Government to pursue his studies for two years. He went first to Heidelberg, where he attended the lectures of Kopp, Kirchoff, and Erlenmeyer, working in Erlenmeyer's laboratory: thence he proceeded to Berlin, to study with Baeyer, and finally to Kolbe, in Leipzig, where he spent most of his leave. Here, in 1866, he made his

researches on the first isomeric acid of the fatty series, which he discovered, namely, *iso*butyric acid and its derivatives. After his return to Kazan he published (1869) his paper, "Ueber die reciproke Beeinflussung der Atome im Molecule." The work described in this memoir, and the ideas contained in it, he always regarded as his most valuable contribution to chemical science. Its importance was pointed out long subsequently by Michael (*J. pr. Ch.*, 1899, [ii], 60, 288). Soon after this Markownikoff became Professor in Kazan, and, on the transference of Butlerow to St. Petersburg, Director of the laboratory. This post he held for four years. In 1871, he and five colleagues resigned for political reasons. Markownikoff, however, immediately received an invitation to occupy the chair of chemistry in the University of Odessa, the Russian universities having at that time the power of making appointments in that way. Here he remained until 1873, when he was called to the University of Moscow. In this stimulating position he found ample scope for a very active mind, and here he produced the greater number of his researches. With much effort he surmounted many very serious difficulties in the building of his new laboratory (1884—6).

Here Markownikoff began his long and laborious investigation of Caucasian petroleum, which occupied him during the last decade of his life. In 1893, a serious misfortune befel him, for he was dismissed from his post without reason assigned, and deprived of his emoluments and official residence. Nevertheless, he continued to work on indefatigably in his own house, assisted by his faithful servant Mikhailo, who had become wonderfully expert in fractional distillation. He died quite unexpectedly, in the midst of his labours, while engaged in preparing some of his results for publication. An apoplectic seizure ended his life in a few hours.

Markownikoff was a conscientious man of science, ever setting exactitude, earnestness, and honour above the ambitions of the moment and the vanities of the self-seeker. In his political opinions he was, to his own severe loss, an outspoken patriot. As a delegate of the Red Cross, he took an active part in the work of disinfection in the Russian Army during the 1878—9 campaign. His numerous pupils, not a few of whom occupy important scientific and technical positions, will long and sincerely lament their distinguished master.

Markownikoff was elected a Foreign Member of the Chemical Society on January 20, 1898, and on February 25, 1901, received the congratulations of the Council on the fortieth anniversary of his doctorate. He was the author of sixty-two papers, and of several separately published memoirs, the most important of which related to Caucasian petroleum (in which work he was associated

with Ogloblin), army disinfecting practice, the plague in Russia, modern chemistry, and chemical industry in Russia.

The investigation of Caucasian petroleum led to the discovery that this substance contains as principal constituents a series of hydrocarbons of peculiar character, to which Markownikoff gave the general name naphthene. They somewhat resemble paraffins in yielding no addition compounds, and by Markownikoff himself were supposed to consist of the hydrides of benzenoid hydrocarbons, a view which is now generally accepted. The lower fractions of this petroleum also contain benzene and a number of its homologues. These discoveries, with the observation of the relation of the expansion coefficient to specific gravity, and of the extraordinary tenacity with which the higher paraffins hold the gaseous ones, even at elevated temperatures, are all matters of great importance to the petroleum industry and its scientific consideration.

Markownikoff also discovered a C_6 glycerol, and made a study of suberone, from which he obtained a monohydric alcohol called suberol, as well as the oxime and a base formed by its reduction. From suberyl iodide by reduction, a saturated hydrocarbon, suberane, C_7H_{14} (heptamethylene), is formed, which is readily converted into the heptanaphthene present in Caucasian petroleum. Papers on many other subjects, such as the pyrotartaric acids, on dichlorohydrin, and on Bulgarian rose-oil, testify to his activity and wide interests.

Markownikoff's association with Kolbe and Erlenmeyer early led him to speculate very deeply on questions of isomerism and allied subjects; ideas of this kind are found in most of his work, and consciously dominated all his scientific thought. There is, as usual in such cases, some difficulty in accurately determining the true share of the teacher and the student. The theoretical results (1869) on which he laid chief stress as his most important contribution to chemical science have already been mentioned. A very clear statement of them, in his own words, will be found in the *Comptes rendus*, 1875, **81**, 668—671. They are at first comprised in two rules:

(1) "Lorsqu' à un hydrocarbure non saturé, renfermant des atomes de carbone inégalement hydrogénés, s'ajoute un acide haloidhydrique, l'élément éléctronégatif se fixe sur le carbone le moins hydrogéné."

(2) "Pour le cas de l'addition des hydracides aux molécules saturées, contenant un élément négatif fixé à celui de ces carbones qui est doublement lié, je me suis permis de donner comme une règle que l'atome de l'élément négatif d'un hydracide se place à côté de son pareil qui s'y trouvait déjà."

Subsequent consideration, and a note of warning from Henry,

induced him to reconsider these rules. For it is clear that the results of chemical change are as much affected by conditions as the process itself, and so must be the molecular structure. Hence the two rules are combined together into the following more perfect expression:

"Lorsqu' à une molecule non saturée C_nH_mX s'ajoute un autre système moléculaire YZ à *une température basse,* l'élément ou le groupe le plus negatif Y se combine avec l'atome de carbone le moins hydrogéné, ou avec celui qui était déjà en liaison directe avec quelqu' élément négatif; mais, à *des températures comparativement plus hautes,* c'est l'élément Z qui se fixe sur le carbone le moins hydrogéné, c'est-à-dire que, pour les mêmes substances, la réaction prend une marche tout à fait opposée à la première."

One sees how much and how long the matter remained in the mind of its author, and how characteristic these "rules" are of his mental atmosphere. Although we cannot assign to Markownikoff a position in the first rank of original thinkers and discoverers, his name will always be associated with unremitting industry, honesty of purpose, and integrity of record.

EDMUND J. MILLS.

LYON PLAYFAIR.

BORN MAY 21ST, 1818; DIED MAY 29TH, 1898.

BY the death of Lord Playfair the Society lost its Senior Past President, and the last survivor of the seventy-five who had founded the Society in 1841. Such a time must come in the history of every society such as ours, but it can only rarely happen that such a passing away from our midst occurs in circumstances so pathetic as with us. The Society had hoped to entertain at a banquet, on June 9th, 1898, no fewer than seven of its Past Presidents who had been on the roll of its Fellows for half a century; but this hope was destined to be blighted by the somewhat sudden death of Lord Playfair on May 29th.

Born at Meerut, in Bengal, on May 21st, 1818, Lyon Playfair was of pure Scottish parentage, his mother having been a Miss Janet Ross, of Edinburgh, whilst his father, Dr. George Playfair, Chief Inspector-General of Hospitals in Bengal, was the eldest son of James Playfair, Principal of the United Colleges of St. Leonard and St. Salvator, in St. Andrews. To this old University city of St. Andrews Lyon and his elder brother George were sent home in 1820 to be educated, first under a governess, then at the parish

school, of which he always spoke highly, then at the Grammar School, where he was taught "Latin, and nothing but Latin." At the age of fourteen he was sent to the University, and whilst there at this early age, both he and his brother gave indications of the lines with which they were to be more or less identified in after life; being found fault with by their mother for spending so much time in the kitchen one day, it was found that George was boiling a sparrow in order to obtain its skeleton, whilst Lyon was endeavouring to prepare sugar from beetroot.

After a short time spent in the office of his merchant-uncle, James Playfair, in Glasgow, we find him, in 1835, commencing his medical studies, and as chemistry was already his favourite pursuit, he preferred to study under Thomas Graham at the Andersonian College rather than at Glasgow University. Two of his fellow-students at this time were destined to become famous, but in very different ways; one was David Livingstone, the African explorer and missionary, and the other James Young, the founder of the paraffin industry in this country. When Graham left Glasgow to become Professor of Chemistry in University College, London, Playfair went to Edinburgh in order to complete his medical education. Illness, however, compelled him to discontinue the study of medicine, so his father advised him to look to India for a career as others of his family had done. In his nineteenth year we find him, therefore, once more in India, and again trying a mercantile career. His final choice, however, was about to be made, for in 1838, when Graham appointed him his private assistant, he gave up commerce for the pursuit of science. In 1839, Graham recommended him to go to Giessen to study under Liebig, and whilst there he published his first scientific paper "On a New Fat Acid from the Butter of Nutmegs"; this acid he named myristic acid.

Liebig was at this time writing his "Agricultural Chemistry," and arranged with Playfair to translate it into English, and this was done almost simultaneously with the German. As Liebig himself was unable to come over to the meeting of the British Association in Glasgow in 1840, Playfair (who had been appointed one of the Secretaries to the Chemical Section), along with Ettling, Will, and Varrentrapp, came to the meeting, and brought Liebig's views prominently forward.

In 1841 he became chemical manager of the Primrose Calico Printing Works at Clitheroe, and there obtained experience which was to be of the highest value to him in later years. Becoming Honorary Professor of Chemistry in the Royal Institution in Manchester, he soon had more pupils than he could accommodate, and had amongst the visitors at his lectures the veteran John Dalton. The offer of

the Professorship of Chemistry at Toronto led to his being induced by the Prime Minister of that day, Sir Robert Peel, to remain in this country, and in 1845 he was appointed Chemist to the Geological Survey. He began his work as such in a small laboratory in Duke Street, Westminster, where he continued his well-known researches (which he had begun in Manchester), along with Joule, on the atomic volumes of salts; and here he carried out his research resulting in the discovery of the nitroprussides. It was here, also, he had two assistants, Kolbe and Frankland, who were later to be well known to fame.

Fired as he was by the spirit of Liebig's teaching and by his own enthusiasm to carry on research in chemistry for its own sake, and imbued as he was with the great importance of a thorough training in the laboratory for all students who were to do useful work in chemistry, Playfair was not to be allowed to do much along any of these lines. His eminently practical mind and very varied experience marked him out to those in authority as pre-eminently fitted to carry out, on a large scale, the investigation of various problems which were prominently before the public at this time. For example, he was appointed a member of the Royal Commission of 1843 to inquire into the health of towns, and as he was at this time still in Manchester, he took as his district the County of Lancashire; and from the ardent way in which he threw himself into this work, he was before long recognised as a leader in all matters relating to the improvement of the public health. This work was followed by his being asked by the Government to report on the state of Buckingham Palace and of Eton College. Then the Board of Trade wanted a report on graveyards, and analyses of all the water supplies to towns; the Admiralty wanted advice as to what were the best coals for steam navigation. This involved an investigation of the composition of the various kinds of coal, their calorific values, and their evaporative powers under actual steam boilers. An investigation along with De La Beche, on a disastrous explosion in a coal-mine at Jarrow, led to his carrying out the analyses of a large number of samples of "fire-damp." The next important Royal Commission of which he was a member, and one which led to many far-reaching changes politically, was that on the potato disease and famine in Ireland in 1845.

One very important and famous research, undertaken along with Bunsen, in 1844, at the instance of the British Association, was that on the chemical operation of blast furnaces in the manufacture of iron. The investigations were carried out near Alfreton, in Derbyshire, on blast furnaces belonging to Mr. Oakes, of Riddings, whose youngest daughter Playfair married two years later.

In 1848 he was elected a Fellow of the Royal Society, and in the same year we find him in Paris, acting as correspondent to the *Daily News* during the exciting week in June.

Evidence had all along been growing stronger and more conclusive that Playfair's greatest sphere of usefulness lay mainly in the practical application of science to the numerous requirements of the nation, and in 1850 he became associated with what was to be, in many respects, the chief work of his lifetime. Sir Robert Peel had seen much of him in connection with the numerous Royal Commissions of which he had been a member, and with the various scientific and other inquiries he had carried out for the Government and other public bodies. He discovered that Playfair was essentially a practical man and a man of action, who was endowed with an unusual degree of tact, clear-headedness, and knowledge of the world; these, combined with his enthusiasm, enabled him to surmount and triumph over difficulties which would have proved too much for most men. It was the possession of these qualities rather than his knowledge of science in general, or of chemistry in particular, which marked him out as the man for the part he was to play in the organisation of the Great Exhibition of 1851. There can be no doubt that Playfair's experience in commercial affairs and his knowledge of the aims and the difficulties of business men generally were of the utmost value in thoroughly interesting manufacturers of all kinds of products, and in bringing home to them the advantages which would accrue to them through the success of the Exhibition. Until Playfair appeared on the scene they seem to have been, if not actively hostile, at least quite apathetic as a body towards the Exhibition and its aims. How great a success the Exhibition was everyone knows now, and instead of being a financial failure it ended with the handsome profit of £186,000. It may fairly be claimed for Playfair that had it not been for his energy, tact, and business capacity it would have been far otherwise. From the Exhibition to the investment of the profits derived therefrom, and then to his travels on the Continent, inspecting methods of education, especially with regard to the organisation and methods of imparting technical instruction there, to his lectures on Technical Education, and then on to the institution of the Science and Art Department, and the foundation of what is now the Victoria and Albert Museum, the sequence is natural and easily understood. One appointment which particularly interests us is his election, in 1857, as President of the Chemical Society, in succession to Professor W. Allen Miller, and it was peculiarly fitting that it was during his tenure of office that the Society migrated from its rooms

in Cavendish Square to its first set of rooms in Burlington House, which were in the north-east corner. It was during his second year of office that Playfair was appointed to the Professorship of Chemistry in the University of Edinburgh. This he held for ten years, setting to work at once to organise and develop the teaching of practical chemistry especially. Successful as he was in this it was only by the generous expenditure of much of his professorial income that he was able to convert the rooms at his disposal into really useful laboratories for teaching. He left his impress not only on the teaching of chemistry, both in the laboratory and by the clearness of his lectures, but also by the system of stimulating earnest work amongst the students throughout all the university classes by the method of awarding university medals and other prizes in each class. The institution of degrees in science was also very largely due to his initiative and influence.

When, in 1868, members of Parliament were allocated to the Scottish Universities, Playfair was chosen the first member for the Universities of Edinburgh and St. Andrews, a seat which he retained for seventeen years. This was somewhat remarkable, because, himself a pronounced Liberal in politics, he represented what is, and has always been, a well-marked Conservative constituency. This was due to several causes, chiefly, no doubt, to his universally recognised services to the cause and progress of sound education throughout the country, but also in no small measure to his popularity as a Professor in the University, who was brought into contact with large classes of students. But in 1885, recognising that his services were being more and more claimed as a member of the Liberal party, he withdrew his candidature for the representation of the Universities, and was elected member for South Leeds, which constituency he continued to represent until 1892, when, on the recommendation of Mr. Gladstone, he was elevated to the peerage under the style of Baron Playfair of St. Andrews. In 1883 he was appointed a Knight Commander of the Bath, and in 1895 he received the Order of the Grand Cross of the Bath.

Amongst other important work which he was chiefly instrumental in carrying out for the country, although not of especial interest to Fellows of the Chemical Society, were the introduction of halfpenny post-cards, the remodelling of the Civil Service, known as "The Playfair Scheme," his work on the Cattle Plague Commission, and in organising the jury department of the 1862 Exhibition. His tenure of the office of Postmaster-General in 1873 was too short for him to leave much of his mark there, for after three months' work the Liberal Government went out of office.

It need hardly be pointed out that his work on these various

schemes could not always tend to the increase of his popularity, for some were very strenuously opposed, but everyone admitted the honesty of purpose pervading all, however much they differed from him.

The record of original papers standing in Playfair's own name in the Royal Society's catalogue contains the names of twenty-seven papers, of which that on the nitroprussides is perhaps the most important. Other papers which have left their mark on the progress of science were those with Bunsen on the chemistry of blast furnaces, with Joule on the atomic volume of salts, and with J. A. Wanklyn on a method of determining vapour densities at temperatures below the boiling points of the substances.

The amount of original work, however, which Playfair carried out at one time and another cannot be estimated by a record such as that just given, for the numerous investigations on which he was almost continually engaged embodied an enormous amount of work really original in the strictest sense, and demanding scientific qualities of the highest order.

Playfair was three times married, first in 1846, as previously mentioned, to Miss Margaret Oakes, daughter of Mr. Oakes, of Riddings House, near Alfreton, then in 1857 to Miss J. A. Millington, and thirdly, in October, 1878, to Miss Edith Russell, of Boston, U.S.A., now Lady Playfair, who survives him, along with his only son, George James, Lord Playfair, and two daughters.

A. Scott.

ALEXANDER WILLIAM WILLIAMSON.

Born May 1st, 1824; Died May 6th, 1904.

Alexander William Williamson was born at Wandsworth on May 1, 1824. His father, Alexander Williamson, who came to London from Elgin as a boy, married, in 1820, Antonia, daughter of William McAndrew, a Scotchman settled in London as a merchant, and of his wife Antonia (born Sykes), an English lady. Mr. Williamson had three children: Antonia Helen, born in 1822, Alexander William, and a second son, James, who died in childhood. Antonia married a Mr. Clark, and died, a widow, several years before her brother. She combined admirable accomplishments with much force of character and intellectual independence with great kindness of heart. She was untiring in acts of well-considered and persevering benevolence. Although this lady's career forms no part

of the subject of this notice, her qualities of heart and mind are not without interest as throwing an indirect light on the moral and intellectual characteristics of the home in which she and her illustrious brother grew up.

As a child, and throughout his boyhood, young Williamson had very delicate health. The weakness showed itself most obviously in affections of the eyes, the consequence being that his parents, as well as the medical men they consulted, were misled as to the nature of the complaint. Local treatment was adopted, but it only aggravated the evil, and it was not until he was about sixteen that it was fully recognised that what was needed was to let the eyes alone and build up the general health. Eventually, he grew up to vigorous manhood, but the right eye was permanently useless, and the left arm had very little power. It was in spite of these serious physical disadvantages that all his work was accomplished.

Between 1825 and 1831, Mrs. Williamson and her children spent much time at Brighton, where Mr. Williamson, at that time a clerk in the East India House, paid them frequent visits, notwithstanding the somewhat long coach-journey each way which such visits involved in those days. Subsequently, Mr. Williamson bought a house in Wright's Lane, Kensington, with a large garden, now built over. While living here the young Williamsons were much in the company of James Mill's children. John Stuart, the eldest, being older than the future chemist by eighteen years, to say nothing of his abnormally early intellectual development, can hardly have been much of a companion for the sickly boy. Mill was Mr. Williamson's superior officer at the East India House, and it is not an unnatural supposition that it was their common employment there that brought them acquainted. However this may be, the fact that Mr. Williamson was for many years on intimate terms with Mill and came to share, to a great extent, his opinions on religious, social, and educational questions, cannot have been without influence on his son's mental development, seeing that he was thus brought into contact with the innermost circle of the Utilitarians. Another result of this intimacy was that Mr. Williamson became one of the strenuous band of educational pioneers and reformers who, in 1826, founded the University of London, afterwards University College, London, the institution with which his son was destined to be so long and closely connected.

In or about 1840, Mr. Williamson retired from the India House on a pension. He soon afterwards gave up his house at Kensington, and he and his family removed to the Continent, and lived for several years chiefly in France and Germany.

In 1840, young Williamson was entered as a student of the

University of Heidelberg. His father's idea was that he should study medicine, and with this view he attended Leopold Gmelin's lectures on chemistry and those of Tiedemann on anatomy. Very soon, however, he announced his intention of becoming a chemist, an announcement which was by no means favourably received by his father, to whom the only idea which it conveyed was associated with the vision of a shop window with bright lights shining through corpulent blue and yellow bottles. However, the young student was eventually able to explain the real nature of his ambition and to get his father's sanction to the course of study he proposed. In this he was aided by Prof. Gmelin, who, although at first inclined to think the lame arm and the loss of sight of one eye were enough to make a chemical career impossible, was so much impressed by the zeal and intelligence of his pupil that he told his parents he would certainly be a chemist.

In the years of which we are speaking, Giessen was the centre of chemical activity, in a sense that no other place ever was either before or since. The Giessen Laboratory was the first ever built specially for the reception of students, and Liebig's activity and genius and wonderful power of communicating his own enthusiasm to his pupils were creating a new era in chemical training and investigation. Thither Williamson went in April, 1844, and he remained there for two years, living in the house of Prof. Hillebrand, the professor of philosophy. In his first semester, besides working at chemistry, he attended Bischoff's lectures on physiology. In writing to his father, he speaks of the "clear and impressive" style of these lectures, which were delivered at seven o'clock in the morning, and says, "I get up every morning regularly before six without being called." He seems to have been somewhat disappointed with the first lecture he heard from Liebig, finding it "rather tedious from the extreme elementary manner in which he treated it," and he was "not remarkably pleased with his delivery." His stay at Giessen seems to have been marked by great industry: he was enthusiastically interested in his work, and allowed himself no distraction beyond such exercise, chiefly walking, as he felt to be needful for his health. Now and then he took part in a "picnic," and very occasionally he mentions having been at a dance. He was impressed by the earnestness of his fellow-students in the laboratory, and speaks of them as being "a superior class from the generality of Heidelberg students, being come here from all quarters of the globe for scientific purposes and devoting themselves to nothing else." He continues, "the chemists are, accordingly, the principal people here, and are generally much respected." Among Englishmen who were at Giessen in Williamson's time were Hodges,

Blyth, Walter Crum, Brodie, and Sheridan Muspratt. Anderson (of Glasgow) immediately preceded him as an inmate with Prof. Hillebrand.

His work at Giessen resulted in the publication by Williamson of his first contributions to science, namely, "On the Decomposition of Oxides and Salts by Chlorine," "On Ozone," and "On the Blue Compounds of Cyanogen and Iron," which all appeared in the Memoirs and Proceedings of the Chemical Society. The materials for a note "On the Constitution of Œnanthol," published after he left Giessen, were also accumulated there.

In connection with the immense number of investigators whom Liebig trained, and the almost countless researches that issued from his laboratory, it is of some interest to note, as an indication that these results were not attained by hurrying his pupils on prematurely to original work, before they had been thoroughly drilled in routine operations, that when Williamson, a little more than a month after his arrival at Giessen, proposed to examine the lower oxides of iodine, Liebig told him it was a hopeless task, and recommended him to do some ash analyses instead.

A subject which seems to have occupied much of Williamson's thought during his first year at Giessen was the theory of galvanism, which, as set forth by Gmelin, he considered "particularly imperfect, defective, and forced." He thought out and put on paper "a system which seems to me much more simple and natural." In writing to his parents he repeatedly refers to electrical experiments with which he was engaged, and in April, 1845, he speaks of a paper on electricity which he submitted to Liebig, whose reception of it was much more favourable than he had expected, "for it was the theory of Humphry Davy which I had ventured to attack." With Williamson's concurrence, Liebig submitted the paper to Buff. Williamson speaks of Buff as "one who considers as indubitable the fundamental principles which I deny," and he is amusingly warlike in speaking of the advantage he expects to derive from Buff's criticism: "My theory will thus undergo from one personally friendly to me the searching criticism to which it would otherwise first be exposed from the public, and I shall thus be enabled before publication to become better acquainted with the defence of my opponents from a preliminary skirmish. I shall obtain an idea of the method of warfare to be pursued, and shall accordingly be able to arrange and dispose my forces more advantageously for the battle than would otherwise be possible." It does not appear that this paper to which, for the time at least, Williamson attached so much importance was ever published. It is not impossible that Liebig's favourable reception of it indicated rather friendship for the author

and a general high opinion of his powers than agreement with the special views therein set forth. Without apparently committing himself on the scientific question involved, he praised the writer's language and style, and expressed surprise that he should be "able to write in such a manner in German."

Williamson was naturally highly gratified that, in the course of their interview about the electricity paper, Liebig proposed to him that he should take the degree of Doctor of Philosophy, and records, in reference to the particular form of the degree suggested, that "it is an honour which, as I hear, Liebig has as yet conferred only on two persons." The degree seems to have been actually conferred in August.

After the summer of 1845, Williamson suspended for a time his chemical studies in order to devote himself to mathematics and physics. He worked at the former under Zamminer, and at the latter with Buff, who accorded him special facilities and gave him access to the Physical Cabinet. This apparently was what Williamson meant when he said he was allowed "the use of an institution to which no student in Giessen has as yet been allowed access, being only intended for the use of lecturers." At the same time he attended, five times a week, Hillebrand's lectures on "Literaturgeschichte"; these were given in the evening, and "profitably filled up an hour which would probably otherwise be turned to little account."

In the summer of 1846 he went to Paris, and stayed there for three years. His chief occupation during this time was the study of advanced mathematics. John Stuart Mill had recommended Auguste Comte to Mr. Williamson, senior, as the first man in Europe for completing a scientific education, and during his residence in Paris Williamson was Comte's pupil. He had a regular mathematical lesson three times a week, and very often spent his evenings at Comte's house with him and his disciples. His long and intimate association, during the impressionable years of early manhood, with such a man as Comte cannot have been without influence on his subsequent mental characteristics, and it is possible that such an influence may be traced in a certain fondness for generalities that Williamson sometimes showed, and in occasional turns of phraseology.

Notwithstanding his mathematical studies, his mind was still occupied with chemistry. He set up a laboratory in his house in Paris (8 Rue des Francs Bourgeois), and among the results of his work succeeded in producing urea and carbonic acid by the direct oxidation of an amide. These experiments were embodied in a paper which he read to the Italian Scientific Congress at Venice in

1847. He speaks also of having been "engaged in an extensive research, whose object is to elucidate some obscure, though fundamental, chemical phenomena, my views on which were suggested and gradually developed by my former studies." At about the same time he says he intends to "go on with a research on the laws of chemical action." It is perhaps not unlikely that these investigations, which do not seem ever to have been published, may have referred to the views on the interchange of atoms among neighbouring molecules, to which he gave emphatic expression a year or two later.

Early in 1849, Graham made Williamson's acquaintance in Paris, and encouraged him to become a candidate for the professorship of analytical and practical chemistry in University College, London, which was then vacant through the death of its first holder, George Fownes. He applied and was appointed, and entered on his duties in the following October.

At the beginning of his first college session, Williamson read himself in by delivering a public introductory lecture to the courses of the Faculty of Arts and Laws. Of this lecture it is perhaps not unfair to say that the best part of it was the title, "Development of Difference the Basis of Unity." The discourse itself is disappointing, and mostly consists of somewhat obvious generalities set forth with a philosophical air, but coming to no definite point. Graham kindly congratulated the lecturer on his musical voice.

Williamson's first few years at University College constituted a period of remarkable activity and productiveness. The first session of all produced his memorable paper on etherification, and it was soon followed by valuable papers from his pupils: among the earliest, Duffy on stearine and Wills on heptylic alcohol. The session 1853—1854 was particularly fruitful, and furnished no less than six experimental papers by himself and his pupils. At this time he was a splendid teacher, always in the laboratory, going from one student to another, arousing and maintaining their interest in their work, and ready to discuss with them any point on which they sought his help. Now and then, when Graham was obliged to be absent, Williamson would lecture on general chemistry in his stead, and these occasions were always hailed with delight by some of the students to whom he seemed to bring out new points of interest in the best-worn subjects by the freshness of his treatment and the new light he would throw on them. In the laboratory, he abounded in new devices. If there was a traditionally established way of conducting a given operation, this was to him rather a reason for trying a new plan than for doing it in the old way. His new methods were perhaps not always important improvements, but

they at least had the effect of preventing his pupils from falling into a stereotyped routine and thinking that because a thing had been done in one way before it could never be done in any other. He would never admit that an experimental difficulty was insurmountable: "If you know clearly," he would say, "what you want to do, there is always a way of doing it." Kekulé, Odling, and Brodie were constant visitors, and in the talk of these men in Williamson's little room at the end of the laboratory the seed was planted of much of the chemical theory of the day.

Williamson's great achievement was, of course, the theory of etherification. This was first published in a paper read before the British Association at Edinburgh on August 3, 1850, and afterwards printed in the *Philosophical Magazine*, 1850, [iii], **37**, 350—356. A further publication with more details was made two years later in the Quarterly Journal of the Chemical Society. His leading idea in undertaking the research, of which these papers were the outcome, was, starting from common alcohol, to climb up to higher terms of the homologous series. With this view, he dissolved metallic potassium in absolute alcohol, thus replacing one-sixth of the hydrogen in alcohol by potassium, and then substituted ethyl for the potassium by acting on the potassium compound with ethyl iodide. The resulting product was a substance of the anticipated composition, but to his surprise, instead of being a new alcohol, it was nothing more than common ether. The explanation which Williamson himself gave of this result now seems so obvious that it requires some effort to see that an explanation was needed, but at the time it marked a step of immense theoretical importance.

Up to the date with which we are concerned, the prevailing ideas of chemical constitution were still largely influenced by the notion of binary combination which grew up when the only compounds that were at all familiarly known were metallic salts. These were regarded as secondary compounds formed by the union of two primary compounds, a metallic oxide and an (anhydrous) acid. So-called double salts were looked on as tertiary compounds formed by the combination of two secondary compounds. Hydrated acids and bases were supposed actually to contain water, which might be an unavoidable, but was a non-essential, constituent: caustic potash was KO,Aq $(O = 8)$; sulphuric acid was SO_3,Aq. In the same order of ideas, ether was looked on as oxide of ethyl, C_2H_5O, and alcohol as the hydrated oxide, C_2H_5O,HO. It is true that Laurent and Gerhardt had advocated the view that the molecules of these substances must both contain the same quantity of oxygen, namely, one atom of twice the commonly accepted mass; but their arguments, which were to a great extent founded on considerations of

molecular volumes in the state of vapour, were not as yet widely accepted. What Williamson did was, in the first place, to show what was the true genetic relation between ether and alcohol, and to prove, by a process which came as near to an absolute demonstration as is possible in relation to any question of chemical constitution, that the formation of ether from alcohol is due, not to the loss of the elements of water, but to the substitution of the group or radicle C_2H_5 in place of an atom of hydrogen; that the molecules of water, alcohol, and ether all contain the same quantity of oxygen; and that these three substances form a true series in which the relation of the middle term, alcohol, to either of the extremes is the same as that of the other extreme term to it.

He showed, in the second place, that in the ordinary process of etherification of alcohol by sulphuric acid there is an interchange of the group C_2H_5 for hydrogen between the alcohol and the acid, first in one direction and then in the other, and he maintained that this is only a particular example of what goes on in liquids in all cases —that, in fact, the molecules of a liquid are not structures permanently composed of the same individual atoms, but that they are constantly decomposed and reproduced by interchanging atoms with other molecules. If the interchanging molecules are similar, the results of the exchange of atoms are similar to the original molecules; but if molecules of different kinds are present, the interchange gives rise to new combinations: to take the simplest kind of case, an exchange of atoms between molecules of the composition AB and molecules CD gives rise to molecules AD and CB, which, in their turn, reproduce AB and CD. There are thus at any instant molecules of four different kinds in presence of each other, instead of only two, and the apparently constant composition of a finite portion of the mixture results from the number of transformations which take place in one direction in each element of time being sensibly equal to the number taking place in the opposite direction.

A few years later, Clausius was led from a different point of view to similar conclusions, and, as is well known, his views have been developed and applied to the explanation of a great variety of phenomena by Arrhenius and others.

In 1851, the year after the first publication of his paper on etherification, Williamson published a paper "On the Constitution of Salts," in which he worked out further and applied to a great variety of cases the idea already employed in the former paper when he represented the molecules of water, alcohol, and ether as constituted on the same model: $\begin{matrix}H\\H\end{matrix}O$, $\begin{matrix}C_2H_5\\H\end{matrix}O$, $\begin{matrix}C_2H_5\\C_2H_5\end{matrix}O$. The keynote of the present paper was given in the following sentences: "I believe that throughout inorganic chemistry, and for the best-known

organic compounds, one single type will be found sufficient; it is that of water, represented as containing 2 atoms of hydrogen to 1 of oxygen, thus $\begin{matrix}H\\H\end{matrix}O$. In many cases, a multiple of this formula must be used, and we shall presently see how we thereby get an explanation of the difference between monobasic and bibasic acids . . . ." The idea of the *water-type* set forth in this paper was immediately adopted by Gerhardt, Odling, Kekulé, and many of the younger chemists of the time. The then recent discovery of ethylamine by Wurtz, and Hofman's discovery of diethylamine and triethylamine and the corresponding derivatives of aniline, had made chemists familiar with the idea of the existence of a considerable number of compounds the properties and constitution of which were best understood by regarding them as being built up on the same type as ammonia. Williamson pointed out that the mutual relations of a still larger class of substances could be elucidated by considering them as constituted on the type of water. The idea has since become so familiar that no further illustration is required in this place.

In 1854 he communicated to the Royal Society a note on the action of pentachloride of phosphorus on sulphuric acid, the chief result of which was a chloro-hydrate of sulphuryl, intermediate between chloride of sulphuryl and sulphuric acid, as shown by the formulæ:

$$SO_2\begin{matrix}Cl\\Cl\end{matrix}, \qquad \begin{matrix}Cl\\SO_2\\H\end{matrix}O, \qquad \begin{matrix}H\\SO_2\\H\end{matrix}\begin{matrix}O\\O\end{matrix}.$$

Williamson laid stress on the formation of this substance as indicating the bibasic character of sulphuric acid which was not at that time by any means generally recognised. This substance is further of theoretical interest as the first example of the class of compounds recognised as being derived from a *mixed type*. This mode of formulation was afterwards very much employed by Kekulé and others especially to represent the mutual relationship of organic compounds.

The most fundamental point of chemical theory that was under discussion during the years we have been speaking of was the atomic weight of oxygen, or, what was in effect the same thing, whether a molecule of water contained one or two atoms of hydrogen. No question of chemical constitution could be raised which did not directly or indirectly involve this point, and it may be fairly said that no chemist made a more effective contribution towards the decision of the controversy, in the way that has long been universally admitted, than did Williamson by the facts and arguments brought forward in papers we have been considering.

In 1855 Graham resigned the Chair of Chemistry in University College on being appointed Master of the Mint, and Williamson was appointed to succeed him, while still retaining his previous Chair of Analytical and Practical Chemistry. He continued to hold both appointments until 1887, when he retired from the College. He entered upon his extended duties with great energy, spending much labour and money on the preparation and illustration of his lectures, and he induced his former pupil, Dr. (now Sir Henry) Roscoe, to help him by taking for the first session the office of lecture-assistant.

A few words more may be said here about his work at University College. As a teacher he was clear and impressive, and, although in a miscellaneous class largely composed of medical students there were naturally always a good many whose attendance was only perfunctory, those who wanted to learn never found him dull or uninstructive. In the later years especially his time was much in demand by outside scientific bodies—as the Chemical and Royal Societies, the British Association, the Society of Telegraph Engineers (now Institution of Electrical Engineers), of which he was one of the founders, the University of London, and many other organisations, permanent or temporary, besides numberless meetings and committees concerned with the work of the College itself. In the latter connection, his clearness of view and directness in advocating what he considered the wise and right course gave him great influence with his colleagues and the Council. He took a leading part in promoting many important reforms and improvements in the work and organisation of the College, as, for example, the establishment of a Faculty of Science and the introduction of laboratory work for engineering students, thus helping to inaugurate a new system of engineering education, which was soon adopted in every engineering school of the country. He was also one of the foremost in promoting the institution of degrees in science in the University of London. He acted as an examiner for the University for two periods of five years, and was a member of the Senate from 1874.

A natural result of such occupations was that, in the later years of his professorship, he was obliged to entrust the detailed supervision of his laboratory more and more to the care of assistants.

The idea of interchange of atoms between molecules in contact with each other, to which Williamson gave expression in his paper on etherification, long interested him. In the autumn of 1856 he began a series of experiments with the view of investigating the conditions that influenced the rate of change in a particular case. The plan of the first experiments was to expose weighed quantities of

ethyl chloride to prolonged contact with aqueous solutions of silver nitrate of known concentrations at a fixed temperature, and to observe the quantities of silver chloride formed in measured times. During the preparation of ethyl chloride for these experiments, which, however, were never completed, he was severely cut and burned about the face by an explosion, but, fortunately, was not permanently injured.

Soon after 1860 he became much interested in practical applications of science, and for several years he had sanguine hopes of effecting important improvements in the steam engine by the use of steam under very high pressure. A few years later, he bought a piece of land and put up buildings near Willesden Junction, intending to carry on there various chemical processes on a manufacturing scale. He was greatly impressed by the enormous possibilities offered by Siemens's regenerative furnace, and this led to his taking an active part in the Landore Siemens Steel Company.

In conjunction with Dr. W. J. Russell, he devised a process for the analysis of gases, in which the methods of allowing for changes of pressure and temperature were greatly simplified. The general idea was to place close to the tube containing the gas to be measured, so as to be at the same temperature, a second tube containing a constant quantity of air at a pressure somewhat less than that of the atmosphere, and, in making a measurement, first, by raising or lowering this tube, to bring the mercury in it to a fixed mark and so the air to a fixed volume; then to raise or lower the measuring tube so as to bring the mercury in it to the same level as that in the air-tube. It is easy to see that this artifice does away with the necessity for knowing the actual temperature or pressure of the gas to be measured; for, remembering that, for a given sensibly perfect gas, the quantity

$$\frac{pv}{273+t} = \text{constant} \times \text{mass of the gas},$$

it will be seen that, the volume of the fixed quantity of air being made the same at each observation, the ratio $p/(273+t)$ is constant, and applies to the gas under examination as well as to the air; consequently, the mass of the gas is proportional to its volume.

Another suggestion connected with chemical calculations relating to gases which he persistently advocated was to define "one volume" of a gas as meaning 11·19 litres at 0° and under a pressure of 76 cm. mercury, this being the volume under the conditions named of 1 gram of hydrogen, or of an equivalent quantity of any other nearly perfect gas. However useful such a convention might be, it be-

comes unnecessary if it is kept in mind that, for 1 gram of any nearly perfect gas, the value of the quantity

$$\frac{pv}{273+t} = 3094 \frac{\text{mass in grams}}{\text{1 gram-equivalent}}$$

in *all* circumstances, if t is temperature centigrade, v volume in c.c., and p pressure in centimetres of mercury. This is the one numerical datum relating to gases that it is useful for a chemist to remember.

In 1865 Williamson published, through the Clarendon Press, an elementary text-book under the title "Chemistry for Students," a work which has passed through several editions. The aim of the book is thus described in the preface: "This little book is intended to supply to students of chemistry an outline of the most interesting and useful facts pertaining to the science, and of the most important ideas that have been got from a study of those facts.

"The method of exposition differs from that which is adopted in most other treatises of Chemistry; for I describe and compare individual facts, so as to lead the mind of the reader towards general principles, instead of stating general principles first and then proceeding to illustrate them by details."

During the composition of this book he was led to consider carefully various current questions of chemical terminology, and, besides embodying his conclusions in his text, he made them the subject of a paper communicated to the Chemical Society. The points chiefly insisted on in this paper were the systematic use of such names as sodic chloride, argentic nitrate, hydro-potassic sulphate, hydro-disodic phosphate, methylic acetate, and the like, instead of chloride of sodium, &c., and, secondly, the application of the name *acid* to such substances as CO_2, SO_3, N_2O_5 . . . . He called H_2SO_4 hydric sulphate, HNO_3 hydric nitrate . . . . or simply sulphate, nitrate, &c.

By the recommendation of Mr. (now Sir Augustus) Prevost, who was a member of the Council of University College, London, five young Japanese noblemen were put under Williamson's care by Mr. Matheson, of the firm of Jardine, Matheson and Co. This was in November, 1863, at the very beginning of the intercourse between Japan and European science. These young men left their own country at the risk of their lives and some of them under assumed names; they came to England to make a systematic study of European science and civilisation, and they could hardly have met with more kindly and judicious guidance and supervision than they received from Williamson. Three of them, of whom the well-known Marquis Ito was one, lived in his house, one of them for nearly four years, and all on returning to Japan attained positions of influence

and importance. Two or three years later, Prince Satsuma sent over sixteen more young men to study under Williamson's direction; among these were Mori Arinori, afterwards Japanese Minister in Paris and London successively; Yoshida, who became Envoy Extraordinary to Washington; and Sameshima, who died in Paris as Chargé d'Affaires.

In many respects, Williamson was admirably qualified to exercise a beneficial influence on the band of earnest young inquirers who were put under his care. He combined strength and decision of character with sound judgment and much kindliness of feeling, and his standard of personal conduct and honour was uniformly high, while his familiarity with the life of France and Germany, and with many of the leading men of those countries, gave him a wide outlook and a freedom from mere insular prejudices.

After his retirement from his Professorship in 1887, Williamson went to live at Hindhead, near Haslemere, where he built himself a house and interested himself in farming. He only rarely came to London to take part in scientific gatherings, but he continued for several years to attend to the duties of his office as Chief Gas Examiner to the Board of Trade.

This notice cannot be concluded better than by quoting from *Nature* (May 12, 1904) a few lines in which Dr. T. E. Thorpe sketches some of the leading points of Williamson's mind and character:

"Like most original thinkers, he was somewhat tenacious of opinions, and apt to be dogmatic in their utterance. His beliefs were too hardly won to be lightly discarded. But although at times impatient of contradiction, he had too strong a regard for truth, was too sincere and broad-minded a man to persist in any opinion if its unreasonableness was made clear to him. Like Carlyle, his philosophy was largely swayed by his emotions, and, like Carlyle's, his judgments on men and things were apt to be tinctured by the mood of the moment—a fact which may serve to account for seeming inconsistencies in their expression.

"He had a high sense of duty, and of the responsibilities of his position as a representative man of science. Although, like many strong men, fond of power, he was in no sense a self-seeking man, and was contemptuous of the artifices by which smaller and more ambitious men seek to gain preferment."

Williamson married, in 1855, Emma, third daughter of Thomas Hewitt Key, F.R.S., Headmaster of University College School and Professor of Comparative Grammar in University College. He leaves a son, Dr. Oliver Key Williamson, and a daughter, who is married to Dr. A. H. Fison.

He was President of the Chemical Section of the British Association at the meeting at Newcastle in 1863, and again at the Jubilee Meeting at York in 1881; he was President of the Association at the Bradford meeting in 1873, and General Treasurer from 1874 to 1891.

He was elected a Fellow of the Royal Society in 1855, and served three times on the Council; he received a Royal Medal in 1862, and was Foreign Secretary from 1873 to 1889.

He joined the Chemical Society in 1848, and was President from 1863 to 1865, and again from 1869 to 1871. He was a Corresponding Member of the Academy of Sciences, Paris, a member of the Berlin Academy, and received honorary distinctions from many other learned bodies, British and foreign.

He died at his house, High Pitfold, Hindhead, on May 6th, 1904.

G. CAREY FOSTER.

LXI.—*The Resolution of Inactive Glyceric Acid by Fermentation and by Brucine.*

By PERCY FARADAY FRANKLAND and EDWARD DONE, M.Sc.

IN a communication by C. Neuberg and M. Silbermann "On *d*- and *l*-Glyceric Acid" (*Ber.*, 1904, **37**, 339), these authors state that by the action of lime on *d*-glucuronic acid they have obtained an optically active glyceric acid, the anhydrous barium salt of which, in aqueous solution, has a specific rotation $[\alpha]_D$ +17·1°, which thus differs most materially from that of the enantiomorphous barium salt described many years ago by one of us (P. Frankland and Appleyard, Trans., 1893, **63**, 299), and for which the value $[\alpha]_D^{12°}$ −10·01° (anhydrous salt) ($c = 10$) was given.

Neuberg and Silbermann further support the new value found by them by resolving inactive glyceric acid by means of brucine and obtaining a barium salt giving, in aqueous solution, $[\alpha]_D$ −17·38° (anhydrous salt) ($c = 7·704$), and remark, "Inasmuch as the barium glycerate, prepared from glucuronic acid, exhibits, under the same conditions, an opposite, but equally large, rotatory power ($[\alpha]_D$ +17·1°), there can be no doubt as to the purity of the compound."

The close coincidence between the rotatory values found by them for the two enantiomorphous barium salts was, indeed, calculated to throw the gravest doubt not only on the previous value obtained by P. Frankland and Appleyard, but inferentially on the optical purity of all the numerous derivatives of active fermentation glyceric acid prepared and described by P. Frankland and his pupils.

The necessity of further investigating these conflicting results was the more cogent as Neuberg and Silbermann supplemented the description of their experiments by the remark that "the experiences of recent years have shown that the preparation of optically active forms by means of biological methods frequently affords no guarantee of the purity of the substances in question, and especially not of complete freedom from the racemic body," a statement which thus attempts to discredit biological methods of preparation in general.

With a view to testing the accuracy of the plausible experimental results and sweeping criticism of Neuberg and Silbermann, we have been obliged to undertake the minute and tedious investigation recorded in the present paper. In this investigation we have succeeded in resolving inactive glyceric acid by means of the fractional crystallisation of the brucine salt, and the results we have obtained confirm the substantial accuracy of the value previously given by P. Frankland and Appleyard for the optical activity of the barium salt. The clue, however, to the much higher and concordant values *for both barium salts* found by Neuberg and Silbermann has only just been furnished by these authors at the end of a paper in the *Zeitschrift für physiologische Chemie*, 1905, **44**, 146, in which they give a new value for the anhydrous barium salt of *l*-glyceric acid $[\alpha]_D$ $+9·9°$, and append a foot-note, in diamond type, in which they state that their previous values of $[\alpha]_D$ $+17·1°$ and $[\alpha]_D$ $-17·38°$ for the anhydrous barium salts of *l*- and *d*-glyceric acids, respectively, prepared by two entirely different methods, were erroneous in consequence of a faulty polarimeter (displacement of the zero of the instrument).

Inasmuch as the erroneous values published by Neuberg and Silbermann have, through the long delay * in their correction, been incorporated in Professor Pope's summary † of Stereochemistry (*Chem. Soc. Annual Reports on the Progress of Chemistry*, 1904, 1, 137), it appears to us of importance that the experimental details on which the quantitative values for the optical activity of the derivatives of *d*-glyceric acid depend should be permanently placed on record to prevent confusion in the future.

The identity which we have proved to exist between the rotation of barium *d*-glycerate prepared from *d*-glyceric acid obtained by the fermentation of calcium *r*-glycerate by means of the *Bacillus ethaceticus* (Frankland and Frew), and that of barium *d*-glycerate prepared from *d*-glyceric acid obtained by resolution of *r*-glyceric acid by means of

* The substance of the results obtained in our reinvestigation was already privately communicated by us to Dr. Neuberg on May 10, 1904; his correction in the *Zeit. physiol. Chem.* is dated Feb. 10, 1905.

† In this summary there is a confusion between *d*- and *l*-glyceric acids. It should be borne in mind that the *d*-acid gives lævorotatory salts, the *l*-acid dextrorotatory salts.

brucine, should further once and for all dispose of the allegations as to the *uncertainty of the biological methods of preparing optically active compounds*, inasmuch as the element of "uncertainty" in polarimetric values is to be sought for in an altogether different quarter.

Experimental.

Barium d-*Glycerate from Fermentation* d-*Glyceric Acid.*

The fermentation calcium glycerate (P. Frankland and Frew, Trans., 1891, **59**, 81 and 96), which was employed as the source of the *d*-glyceric acid, gave the following analytical and polarimetric results:

I. 0·3533 gave 0·1674 $CaSO_4$. Ca = 13·94.
II. 0·3392 „ 0·1611 $CaSO_4$. Ca = 13·97 per cent.

On heating until constant at 130°:

I. 0·2475 lost 0·0310. H_2O = 12·52.
II. 0·2768 „ 0·0346. H_2O = 12·50.
$Ca(C_3H_5O_4)_2,2H_2O$ requires Ca = 13·98; H_2O = 12·58 per cent.

An aqueous solution gave

$$\alpha_D\ -2{\cdot}343^\circ,\ t=17^\circ,\ l=1{\cdot}9984,\ c=10{\cdot}0072,$$
$$[\alpha]_D^{17^\circ}\ -11{\cdot}61^\circ,\ Ca(C_3H_5O_4)_2,2H_2O,$$

which thus agrees with the value previously found by P. Frankland and Appleyard (*loc. cit.*),

$$[\alpha]_D^{17^\circ}\ -11{\cdot}59^\circ.$$

For the preparation of the barium salt, 20 grams of the above active calcium glycerate were dissolved in water and the glyceric acid liberated by the addition of the calculated amount of oxalic acid, the precipitated calcium oxalate being removed by filtration. To the filtrate, a slight excess of pure baryta was added and carbon dioxide passed through the solution to saturation. The liquid was concentrated almost to a syrup, and, after filtering off the precipitated barium carbonate, poured into a large volume of absolute alcohol. The barium glycerate separates as a waxy mass which gradually hardens on standing for several days in contact with the alcohol. A more crystalline product is obtained by dissolving the waxy mass in a very small volume of water, adding absolute alcohol until a slight turbidity appears in the hot solution, when, on allowing it to cool slowly, the barium salt separates in shining plates.

The crystals, after being air-dried for several days, gave the following rotation in aqueous solution:

$$\alpha_D\ -1{\cdot}954^\circ,\ t=20^\circ,\ l=1{\cdot}9984,\ c=10,$$
$$[\alpha]_D^{20^\circ}\ -9{\cdot}772^\circ,\ Ba(C_3H_5O_4)_2,2H_2O.$$

The rotation was also taken in a solution of about the same concentration as that employed by Neuberg and Silbermann (*Ber.*, 1904, **37**, 340):

$$\alpha_D\ -1{\cdot}582^\circ,\ t=20^\circ,\ l=1{\cdot}9984,\ c=7{\cdot}7024,$$
$$[\alpha]_D^{20^\circ}\ -10{\cdot}28^\circ,\ Ba(C_3H_5O_4)_2,2H_2O.$$

Another specimen of the barium salt, prepared in the same way but recrystallised three times, gave:

$$\alpha_D\ -1{\cdot}959^\circ,\ t=20^\circ,\ l=1{\cdot}9984,\ c=9{\cdot}892,$$
$$[\alpha]_D^{20^\circ}\ -9{\cdot}908^\circ,\ Ba(C_3H_5O_4)_2,2H_2O.$$
$$-10{\cdot}93^\circ\ \text{(for the anhydrous salt).}$$

I. 0·3851 gave 0·2348 $BaSO_4$. Ba = 35·89.
II. 0·3960 „ 0·2410 $BaSO_4$. Ba = 35·83.
III. 0·2728 „ 0·1658 $BaSO_4$. Ba = 35·77.
IV. 0·3900 „ 0·2370 $BaSO_4$. Ba = 35·77 per cent.

On heating until constant at 130°:

I. 0·3365 lost 0·0310. H_2O = 9·22.
II. 0·4718 „ 0·0435. H_2O = 9·22.
III. 0·4220 „ 0·0380. H_2O = 9·00.
$Ba(C_3H_5O_4)_2,2H_2O$ requires Ba = 35·83; H_2O = 9·39 per cent.

The salt was also heated until constant at 130° and then submitted to analysis:

I. 0·3069 gave 0·2062 $BaSO_4$. Ba = 39·56.
II. 0·4293 „ 0·2883 $BaSO_4$. Ba = 39·53.
III. 0·3840 „ 0·2580 $BaSO_4$. Ba = 39·55.
$Ba(C_3H_5O_4)_2$ requires Ba = 39·56 per cent.

These figures leave, therefore, no doubt as to the chemical purity of the barium salt obtained from the fermentation of calcium glycerate, whilst the specific rotation, although substantially similar to that previously found by P. Frankland and Appleyard, is a little higher, probably in consequence of the greater purity of the barium salt, which had not before been obtained in such a perfectly crystalline condition.

Attempt to further resolve by means of Brucine the Active Glyceric Acid obtained by Fermentation.

First Experiment.—To a solution containing 33 grams of brucine, dissolved in the least possible quantity of hot ethyl alcohol, were added 7 grams of active glyceric acid. On standing for 24 hours, only a few nodules had separated, but, on stirring, a large quantity of brucine salt was precipitated. The latter was twice recrystallised

from absolute alcohol, then dissolved in the least possible quantity of water and decomposed with a slight excess of baryta. After standing overnight, the brucine was filtered off and the solution repeatedly shaken with chloroform to remove the alkaloid remaining in solution. The liquid was then saturated with carbon dioxide, concentrated, and the barium carbonate filtered off. The barium glycerate was precipitated with alcohol, and, after being air-dried for several days, gave the following results :

I. 0·3700 gave 0·2262 $BaSO_4$. Ba = 35·99.
II. 0·3755 ,, 0·2293 $BaSO_4$. Ba = 35·95.
$Ba(C_3H_5O_4)_2,2H_2O$ requires Ba = 35·83 per cent.

The rotation in aqueous solution was :

$$\alpha_D^{20^\circ} \ -1{\cdot}934^\circ,\ l = 1{\cdot}9984,\ c = 10{\cdot}0048,$$
$$[\alpha]_D^{20^\circ} \ -9{\cdot}679^\circ,$$
$$-10{\cdot}68^\circ \text{ (for the anhydrous salt).}$$

The salt was then recrystallised, after which :

$$\alpha_D^{20^\circ} \ -1{\cdot}933^\circ,\ l = 1{\cdot}9984,\ c = 10{\cdot}0248,$$
$$[\alpha]_D^{20^\circ} \ -9{\cdot}656^\circ,$$
$$-10{\cdot}66^\circ \text{ (for the anhydrous salt).}$$

It was thus evident that the brucine had not further resolved the active glyceric acid obtained by the fermentation of inactive calcium glycerate with the Bacillus ethaceticus.

Second Experiment.—This was carried out on the same lines as the first, but with no less than 20 grams of active glyceric acid and 88 grams of brucine. The brucine salt was recrystallised four times from alcohol under the precise conditions which we had found effective in resolving inactive glyceric acid (see p. 623). The barium salt obtained had, however, again the same rotation in aqueous solution. Thus :

$$\alpha_D^{20^\circ} \ -1{\cdot}589^\circ,\ l = 1{\cdot}9984,\ c = 8{\cdot}2088,$$
$$[\alpha]_D^{20^\circ} \ -9{\cdot}685^\circ,$$
$$-10{\cdot}69^\circ \text{ (for the anhydrous salt).}$$

Resolution of Inactive Glyceric Acid by means of Brucine.

First Experiment.—Twenty-five grams of inactive glyceric acid (Kahlbaum) were added to 110 grams of brucine dissolved in the least possible amount of hot absolute alcohol. After standing for 24 hours, the brucine salt separated on stirring. It was filtered off and recrystallised four times from absolute alcohol, the solution each time being allowed to stand overnight. The salt was then dissolved in water, decomposed with a slight excess of baryta, and the further

purification of the barium salt carried out as already described on p. 622. The air-dried barium salt gave the following rotation in aqueous solution :

$$\alpha_D^{20^\circ} - 1{\cdot}983^\circ,\ l = 1{\cdot}9984,\ c = 9{\cdot}9868,$$
$$[\alpha]_D^{20^\circ} - 9{\cdot}938^\circ,$$
$$- 10{\cdot}97^\circ \text{ (for the anhydrous salt).}$$

Thus by means of brucine a resolution of the inactive glyceric acid had been accomplished, and the barium salt prepared from the more insoluble of the two brucine glycerates exhibited practically the same specific rotation in aqueous solution (– 10·97°) *as the barium salt* (– 10·93°) *prepared from the active fermentation glyceric acid.*

Second Experiment.—In this case, the inactive glyceric acid was obtained from 80 grams of Kahlbaum's inactive calcium glycerate (this being the material which had always been used in the preparation of the active glyceric acid by fermentation); 264 grams of brucine were employed in the same manner as described above (p. 622). The brucine salt was recrystallised six times from alcohol. On preparing the barium salt, we were astonished to find that it was inactive and that it had a distinctly different appearance from the active salt, for even after recrystallisation it could not be obtained in shining plates.

Putting aside the remote possibility that the calcium glycerate used was not really glycerate at all, two explanations of this anomalous result suggested themselves. Either in consequence of the accidental conditions under which the crystallisation of the brucine salt took place no resolution had occurred, or racemisation had been brought about during the preparation of the barium salt.

In order to see whether concentrating solutions of the barium salt led to racemisation, we evaporated a solution of active barium glycerate no less than twelve times to dryness on the water-bath, but found that no racemisation had occurred, whilst in order to ascertain whether the excess of baryta might exert a racemising effect, we evaporated a solution of active barium glycerate with excess of baryta several times, but found that no sensible diminution in the rotatory power had taken place.

We concluded, therefore, that the failure to obtain a resolution must have been due to accidental conditions (probably of temperature) prevailing during the separation of the brucine salt.

Third Experiment.—(Separation of brucine glycerate under definite conditions of temperature.) Thirty grams of inactive glyceric acid obtained from inactive calcium glycerate (Kahlbaum) were added to a saturated solution of 132 grams of brucine in absolute alcohol. The beaker containing the hot solution of brucine salt was placed in a large water-bath at the same temperature, the surface of the water in

the bath being at the same level as that of the liquid in the beaker. The whole was allowed to cool down together, the liquid in the beaker being stirred every five minutes to prevent the formation of a supersaturated solution.

The brucine glycerate was in this way recrystallised four times: on the first two occasions, the separation took place between 20° and 18°, whilst on the last two crystallisation began at 40°, but the temperature was not allowed to fall below 18°. The time taken over each crystallisation was four hours, and during the night the brucine salt was always left on a porous plate to prevent any further separation of crystals at a lower temperature.

The air-dried barium salt prepared from the brucine salt gave the following rotation in aqueous solution:

$$\alpha_D^{20^\circ} - 1{\cdot}917^\circ,\ l = 1{\cdot}9984,\ c = 9{\cdot}92,$$
$$[\alpha]_D^{20^\circ} - 9{\cdot}67^\circ,$$
$$- 10{\cdot}67^\circ \text{ (for the anhydrous salt).}$$

The failure to obtain a resolution in the second experiment is of special interest in connection with the recent clear exposition by Meyerhoffer (*Ber.*, 1904, **37**, 2604) of the temperature conditions which are necessary for the resolution of a racemoid acid by an active base or of a racemoid base by an active acid, and in view of which it is very important that the precise conditions should be recorded under which such resolutions have been successful or the reverse.

Summary of Results.

The barium salt of *d*-glyceric acid has been prepared by us in four different ways, and the several products have yielded the following polarimetric values in aqueous solution:

I. From active calcium glycerate (obtained by fermentation with the *Bacillus ethaceticus*):

$$c = 10{\cdot}00,\ [\alpha]_D^{20^\circ} - 9{\cdot}772^\circ,\ Ba(C_3H_5O_4)_2,2H_2O,$$
$$- 10{\cdot}78^\circ \text{ (anhydrous salt).}$$

Another specimen gave:

$$c = 9{\cdot}892,\ [\alpha]_D^{20} - 9{\cdot}908^\circ,\ Ba(C_3H_5O_4)_2,2H_2O,$$
$$- 10{\cdot}93^\circ \text{ (anhydrous salt).}$$

II. From active calcium glycerate (obtained by the fermentation method), after attempting to effect further resolution by means of brucine:

$$c = 10{\cdot}0048,\ [\alpha]_D^{20^\circ} - 9{\cdot}679^\circ,\ Ba(C_3H_5O_4)_2,2H_2O,$$
$$- 10{\cdot}68^\circ \text{ (anhydrous salt).}$$

Another specimen gave:

$c = 8{\cdot}2088$, $[\alpha]_D^{20°}$ $-9{\cdot}685°$, $Ba(C_3H_5O_4)_2,2H_2O$,
$-10{\cdot}69°$ (anhydrous salt).

III. From inactive glyceric acid (Kahlbaum), by resolution with brucine:

$c = 9{\cdot}9868$, $[\alpha]_D^{20°}$ $-9{\cdot}938°$, $Ba(C_3H_5O_4)_2,2H_2O$,
$-10{\cdot}97°$ (anhydrous salt).

IV. From inactive calcium glycerate (Kahlbaum), by resolution with brucine:

$c = 9{\cdot}92$, $[\alpha]_D^{20°}$ $-9{\cdot}67°$, $Ba(C_3H_5O_4)_2,2H_2O$,
$-10{\cdot}67°$ (anhydrous salt).

These results conclusively prove that the active fermentation glyceric acid of P. Frankland and Frew is pure *d*-glyceric acid and identical with that obtainable by the resolution of inactive glyceric acid with brucine.

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LXII.—C-*Phenyl*-s-*triazole*.

By GEORGE YOUNG.

IN a previous communication, in conjunction with Mr. Oates (Trans., 1901, **79**, 665), I described the preparation of 3-phenyl-1-methyl-5-hydroxy-1 : 2 : 4-triazole, $\begin{matrix}N{\cdot}NMe\\ \|\\ CPh{\cdot}N\end{matrix}\!\!>\!C{\cdot}OH$, and, on heating this substance with phosphorus pentasulphide, a product was obtained, the empirical formula for which contained CH_2 less than that required for 3-phenyl-1-methyl-*s*-triazole. As this was in agreement with the experience of Andreocci (*Atti R. Accad. Lincei*, 1890, [iv], **6**, ii, 209), who obtained 1-phenyl-3-methyl-1 : 2 : 4-triazole, $\begin{matrix}NPh{\cdot}N\\ |\\ CH:N\end{matrix}\!\!>\!C{\cdot}Me$, by heating 1-phenyl-3 : 4-dimethyl-5-oxy-4 : 5-dihydro-1 : 2 : 4-triazole,

$$\begin{matrix}NPh{-}N\\ |\\ CO{\cdot}NMe\end{matrix}\!\!>\!CMe,$$

with phosphorus pentasulphide, we ascribed to our product the constitution of *C*-phenyl-*s*-triazole, $\begin{matrix}N{-}NH\\ \|\\ CPh{\cdot}N\end{matrix}\!\!>\!CH$. This view of the

constitution is now confirmed, as the product obtained on heating *C*-phenylhydroxy-*s*-triazole, $\begin{matrix} N\text{--}NH \\ \| \\ CPh\cdot N \end{matrix}\!\!>\!C\cdot OH$ (Young and Witham, Trans., 1900, **77**, 226), with pentasulphide is found to be identical with the substance obtained from 3-phenyl-1-methyl-5-hydroxy-1 : 2 : 4-triazole.

The term *s*-triazole is used in this paper to distinguish the triazole, which may be either $\begin{matrix} NH\cdot N \\ | \\ CH:N \end{matrix}\!\!>\!CH$ or $\begin{matrix} N\text{---}N \\ \| \\ CH\cdot NH \end{matrix}\!\!>\!CH$, from *v*-triazole, which may be $\begin{matrix} NH\cdot N \\ | \\ N:CH \end{matrix}\!\!>\!CH$ or $\begin{matrix} N\cdot NH \\ \| \\ N\text{-}CH \end{matrix}\!\!>\!CH$.

It is worth noting that, whereas the melting point of 1-phenyl-1 : 2 : 4-triazole, $\begin{matrix} NPh\cdot N \\ | \\ CH:N \end{matrix}\!\!>\!CH$ (m. p. 47°; Andreocci, *Ber.*, 1892, **25**, 225), follows Wedekind's rule (*Ber.*, 1898, **31**, 949) for the effect of substitution on the melting points of carbon-nitrogen cyclic compounds, both *C*-phenyl-*s*-triazole, $\begin{matrix} N\text{--}NH \\ \| \\ CPh\cdot N \end{matrix}\!\!>\!CH$ (m. p. 119·5—120°; this paper), and 1-phenyl-1 : 3 : 4-triazole, $\begin{matrix} N\text{---}N \\ \| \\ CH\cdot NPh \end{matrix}\!\!>\!CH$ (m. p. 121°; Pellizzari and Massa, *Atti R. Accad. Lincei*, 1901, [v], **10**, i, 363), melt at almost the same temperature as the parent substance, *s*-triazole (m. p. 120—121°; Andreocci, *loc. cit.*).

Experimental.

C-Phenylhydroxy-*s*-triazole (6 grams) was intimately mixed with phosphorus pentasulphide (15 grams) and the mixture heated in an oil-bath for 6 hours at 230—250°. The product was boiled with aqueous potassium carbonate in a reflux apparatus, and, after cooling, was extracted repeatedly with ether. The ethereal solution was then concentrated until crystallisation commenced, when, on cooling, the residual liquid crystallised to a mass of shining plates and needles, which melted at 119—120°.

0·1825 gave 0·4426 CO_2 and 0·0809 H_2O. C = 66·14; H = 4·92.
0·1740 „ 43·6 c.c. moist nitrogen at 18° and 761 mm. N = 28·96.
$C_8H_7N_3$ requires C = 66·21; H = 4·83; N = 28·97 per cent.

C-Phenyl-*s*-triazole was readily soluble in alcohol, warm ether, or benzene, and moderately so in hot water, but dissolved only to a slight extent in light petroleum; it crystallised from water in clusters of soft, matted needles, from a mixture of benzene and light petroleum in nodular aggregates of microscopic needles, and from dilute alcohol in slender needles. It melted at 119·5—120°, volatilised in shining

plates when heated over its melting point, and was slightly volatile in a current of steam.

A mixture of equal parts of the products obtained from 3-phenyl-1-methyl-5-hydroxy-1 : 2 : 4-triazole and from *C*-phenylhydroxy-*s*-triazole respectively melted at 119—119·5°.

Towards aqueous alkali hydroxides and towards silver nitrate, *C*-phenyl-*s*-triazole exhibited the behaviour characteristic of those triazoles in which the *N*-hydrogen atom is not substituted. It dissolved in dilute aqueous potassium hydroxide more readily than in water, and was reprecipitated from the alkaline solution on addition of ammonium acetate and expulsion of the liberated ammonia by gentle warming. When treated with silver nitrate in alcoholic solution, it formed the *additive* compound of silver nitrate and the silver derivative, $C_8H_6N_3Ag,AgNO_3,H_2O$, which was obtained as a white precipitate from which H_2O was driven off at 110°.

0·8184, at 110°, lost 0·0352 H_2O. $H_2O = 4·30$.

0·8184 gave 0·4024 Ag. Ag = 49·17.

$C_8H_6N_3Ag,AgNO_3,H_2O$ requires Ag = 49·34; $H_2O = 4·11$ per cent.

C-Phenyl-*s*-triazole dissolved readily in cold dilute or in warm concentrated hydrochloric acid. The *hydrochloride*, which crystallised in slender needles on cooling the solution in the concentrated acid, decomposed on drying or on treatment with water. On adding platinic chloride to the solution in warm concentrated hydrochloric acid and cooling, the *platinichloride*, $(C_8H_7N_3)_2,H_2PtCl_6,3H_2O$, separated in yellowish-red plates containing 3 mols. of water of crystallisation, which were driven off at 110°. The anhydrous *platinichloride* melted and decomposed at 223°.

1·2298, at 110°, lost 0·0912 H_2O. $H_2O = 7·41$.

0·7730, dried at 110°, gave 0·2138 Pt. Pt = 27·66.

$(C_8H_7N_3)_2,H_2PtCl_6,3H_2O$ requires $H_2O = 7·16$ per cent.

$(C_8H_7N_3)_2,H_2PtCl_6$ „ Pt = 27·86 „

When washed with water, the platinichloride lost 2 mols. of hydrochloric acid and was converted into the *derivative*,

$$(C_8H_7N_3)_2,PtCl_4,3H_2O,$$

which is of a lighter yellow colour. This salt lost $3H_2O$ at 110°, dissolved in aqueous potassium carbonate, and was precipitated unchanged from this solution on the addition of hydrochloric acid.

0·6007, at 110°, lost 0·0468 H_2O. $H_2O = 7·79$.

0·5561, dried at 110°, gave 0·1736 Pt. Pt = 31·22.

0·5433, precipitated from aqueous potassium carbonate and dried at 110°, gave 0·1699 Pt. Pt = 31·27.

$(C_8H_7N_3)_2,PtCl_4,3H_2O$ requires $H_2O = 7·93$ per cent.

$(C_8H_7N_3)_2,PtCl_4$ „ Pt = 31·10 „

The *acetyl* derivative, $C_8H_6N_3{\cdot}C_2H_3O$, was obtained by boiling *C*-phenyl-*s*-triazole with acetic anhydride and sodium acetate; it dissolved readily in alcohol, ether, benzene, or warm light petroleum; from its solution in the last solvent, it crystallised in feathery aggregates of slender needles. When recrystallised from dilute alcohol, it formed small, white needles which melted at 90°. It was easily hydrolysed by boiling aqueous potassium carbonate to *C*-phenyl-*s*-triazole melting at 119—120°.

0·2242 gave 43·2 c.c. moist nitrogen at 15° and 754 mm. N = 22·38.
$C_8H_6N_3{\cdot}C_2H_3O$ requires N = 22·46 per cent.

The carbamido-derivative of *C*-phenyl-*s*-triazole, described in the previous paper (Trans., 1901, **79**, 665), was also prepared by the action of potassium cyanate and hydrochloric acid on *C*-phenyl-*s*-triazole obtained from *C*-phenylhydroxy-*s*-triazole. After solution in benzene and precipitation by adding light petroleum, it melted at 147°. The analysis shows that it probably contained traces of unchanged phenyltriazole.

0·1818 gave 0·3855 CO_2 and 0·0818 H_2O. C = 57·83; H = 4·09.
$C_8H_6N_3{\cdot}CO{\cdot}NH_2$ requires C = 57·44; H = 4·25 per cent.

The carbamido-derivative was easily hydrolysed by boiling water or by cold dilute hydrochloric acid with evolution of carbon dioxide and formation of phenyltriazole, which melted at 119°.

LXIII.—*Isomeric Salts of the Type* $NR_1R_2H_3$. *A Correction. Isomeric Forms of* d-*Bromo- and* d-*Chlorocamphorsulphonic Acids.*

By Frederic Stanley Kipping.

The further investigation of the isomeric α- and β-salts which the author obtained by combining *d*-α-bromo- and *d*-α-chloro-camphorsulphonic acids with *dl*- and with optically active bases such as hydrindamine (Trans., 1900, **77**, 861 *et seq.*; 1903, **83**, 873), benzylhydrindamine (Kipping and Hall, Trans., 1901, **79**, 430), methylhydrindamine (Tattersall and Kipping, Trans., 1903, **83**, 918), and *l*-menthylamine (Tutin and Kipping, Trans., 1904, **85**, 65), has brought to light the fact that the isomerism of these compounds is not determined by a difference in the arrangement in space of the groups united with the quinquevalent nitrogen atom; the suggested explana-

tion of the existence of these isomerides, therefore, is now proved to be incorrect.

In one of the most recent papers on this subject (Trans., 1903, **83**, 937), the following statements were made: the β-form of the *l*-hydrindamine salt of the chloro-acid gives, with concentrated hydrochloric acid, crystals of the hydrochloride of the *l*-base, and when, by adding water and evaporating several times to expel hydrochloric acid, this hydrochloride is reconverted into the chlorocamphorsulphonate, the original βl-isomeride is recovered unchanged (*loc. cit.*, p. 943). When, however, the hydrochloride obtained from the βl-form of the bromo-salt is converted into platinichloride and this salt is separated from the bromo-acid and treated with hydrogen sulphide, the regenerated hydrochloride gives with the ordinary ammonium salt of the bromo-acid the α-form of *l*-hydrindamine bromocamphorsulphonate (*loc. cit.*, p. 944).

In order to account for this transformation of the β- into the α-salt, it was suggested that intramolecular change might occur during the formation and decomposition of the platinichloride and thus the arrangement of the groups around the nitrogen atom might be modified. Even at the time, however, this suggestion did not seem to be a very plausible one, and it was stated that further experiments on this point would be made.

Shortly afterwards, a careful investigation of the *d*-bromocamphorsulphonates of various piperidine derivatives failed to reveal the existence of isomeric salts (Barrowcliff and Kipping, Trans., 1903, **83**, 1141), and experiments on the *d*-bromo- and *d*-chloro-camphorsulphonates of *l*-phenylethylamine (*loc. cit.*, p. 1147) also led to negative results; these facts seemed to afford additional and absolutely conclusive evidence that the isomerism of the hydrindamine salts was, in fact, of the nature suggested and in no way determined by the occurrence of isomeric forms of the bromo- and chloro-camphorsulphonic acids.

In spite of this apparently convincing evidence of the homogeneity of the acids in question and also of the further fact that many other workers (Walden, Pope, Wedekind, Lapworth, Jones) had used the *d*-bromo-acid without obtaining the slightest indication of the presence of an isomeride, a fresh investigation of this acid was undertaken.

Some years ago, when the isomeric hydrindamine salts were first discovered, the ammonium salt, prepared from the "pure" acid,* had been repeatedly crystallised and examined polarimetrically, and the aniline salt had also been investigated, but both appeared to be homogeneous; later, in crystallising the *crude* ammonium salt, it is true that a small quantity of a salt not derived from *d*-bromocamphor-

* Acid which had been obtained from the "pure" ammonium salt as originally described by Kipping and Pope.

sulphonic acid was isolated by the author from the last mother liquors, and the same compound was discovered and studied by Harvey and Lapworth (Proc., 1902, **18**, 142), but this substance was easily removed from the main product and could not be contained in the purified salt ordinarily used for the preparation of the acid.

In a much more recent investigation of this ammonium *d*-bromocamphorsulphonate, the results of which have not hitherto been recorded, a large quantity of the salt was first purified by two or three crystallisations, and was then separated into a number of fractions by crystallising it systematically from water; the first and last of these, when examined polarimetrically in 2·5 per cent. aqueous solution, gave $[\alpha]_D$ 83·6° = $[M]_D$ 275° and $[\alpha]_D$ 83·8° = $[M]_D$ 275·6° respectively. The salt was then decomposed with baryta, the ammonia expelled, the acid prepared from the barium salt and again neutralised with ammonia; the whole of this specimen of ammonium salt was then systematically crystallised and separated into eight fractions, each of which had been crystallised several times; the first and last, when examined optically in 2·5 per cent. aqueous solution, gave $[\alpha]_D$ + 84·6° = $[M]_D$ 278° (also $[\alpha]_D$ 85° = $[M]_D$ 279°) and $[\alpha]_D$ 84·8° = $[M]_D$ 278·5° respectively.

In these experiments, therefore, in which the acid had been submitted to almost exactly the same treatment as in those which were used in the study of the isomeric hydrindamine salts ("Regeneration of the Salts," compare Trans., 1903, **83**, 884 *et seq.*), the greatest observed difference in molecular rotation was 4°, which is well within the limits of experimental error; in the case of the *αl*- and *βl*-hydrindamine salts, the difference was found to be 90° (*loc. cit.*, p. 944).

The study of the *cis-π*-camphanates of *d*- and of *l*-hydrindamine, which had also been in progress in the meantime, only served to confirm the conclusion that the existence of the isomeric salts was independent of any isomerism of the bromo- and chloro-camphorsulphonic acids.

Cis-π-camphanic acid (Trans., 1896, **69**, 943) is a substance so easily identified by its highly characteristic crystalline character that any appreciable quantity of an isomeride or impurity in this substance could hardly escape immediate detection, and yet this acid gave with *dl*-hydrindamine approximately equal quantities of isomeric partially racemic salts (Trans., 1898, **73**, 903), both of which, when decomposed with hydrochloric acid, gave the characteristic crystals of *cis-π*-camphanic acid.

Further, it was found (Proc., 1903, **19**, 286) that the salt obtained by combining *cis-π*-camphanic acid with pure *d*-hydrindamine is a mixture, as is also that obtained from the corresponding *l*-base, and that these compounds are not identical with the salts previously described as partially racemic.

Hence the formation of isomeric compounds, apparently analogous

to those derived from the bromo- and chloro-acids, seemed to be definitely established, and as there is so little relationship between the sulphonic acids on the one hand and *cis*-π-camphanic acid on the other, the fact that isomerides were obtained from both seemed to exclude the possibility of this being due to any peculiarity of the acids themselves.

It will perhaps be admitted that a critical consideration of the whole of the evidence—only part of which has been referred to very briefly—pointed strongly to the conclusion that the isomerism of these salts was caused by a difference in the arrangement of the groups around the nitrogen atom; a great array of experimental data could be quoted in favour of this view,* whereas only one fact of importance could be brought forward against it, namely, that the molecular rotations of the bromo- and chloro-salts (not, however, those of the *cis*-π-camphanates) were abnormal; even this fact seemed to have little bearing on the possible existence of isomeric acids, as the molecular rotations of the β-salts of the bromo-acid were *lower*, those of the β-salts of the chloro-acid *higher*, than the "normal" values obtained for the compounds of the α-series.

The discovery of the true course of the isomerism in the case of the halogensulphonic acids was made during some recent attempts to transform βl-hydrindamine bromocamphorsulphonate into the βl-chlorocamphorsulphonate. The first named salt was gently warmed with excess of concentrated hydrochloric acid; the solution was then left at the ordinary temperature to crystallise and the precipitated hydrochloride separated. The filtrate from this salt was then repeatedly evaporated with water to expel hydrochloric acid, and the solution, which now contained hydrindamine bromocamphorsulphonate, mixed with excess of the bromo-acid, left to crystallise; the bromo-salt thus obtained, which had doubtless been in part produced from the hydrochloride, had a specific rotation $[\alpha]_D + 38{\cdot}5^\circ$ in two per cent. aqueous solution, and consisted therefore of the original βl-isomeride in a pure condition (*loc. cit.*, p. 897). The crystals of the hydrochloride which had been separated were now repeatedly evaporated with chlorocamphorsulphonic acid, in the expectation of obtaining the βl-chloro-salt, but on crystallising the residue from water, the αl-chloro-salt was obtained, apparently (not really) free from βl-isomeride.

At first, it seemed possible that the βl-bromo-salt might correspond with the αl-chloro-salt, these being the isomerides having the lower

* Aschan (*Zeit. physikal. Chem.*, 1903, **46**, 293), discussing the author's work, writes as follows: Dagegen haben die von Kipping und seinen Schülern über das Hydrindamin und einige andere, gleich konstituierte Basen ausgeführten bemerkenswerten Untersuchungen entschieden zu dem Schluss geführt, dass Verbindungen des Typus Na_3bc stereoisomer auftreten können.

molecular rotations, in which case the *ad*-bromo-salt should give the *βl*-chloro-salt when treated in the manner just indicated; experiment, however, showed that this was not so, and that all the salts of the β-series, as well as those of the α-series, when transformed into the hydrochlorides and then treated with bromo- or chloro-camphorsulphonic acid, or the corresponding ammonium salt, gave invariably the isomeride of the α-series as the main product.

Here then was the clue to the mystery. The hydrochloride prepared from a β-salt gives the α-salt when it is treated with bromocamphorsulphonic acid from a bottle; when, however, it is evaporated with the bromo-acid which the β-salt originally contained, it yields the pure β-salt.

There are, therefore, two isomeric *d*-bromocamphorsulphonic acids, one of which is contained in the α-salts and in ordinary ammonium *d*-bromocamphorsulphonate, the other in the hydrindamine salts of the β-series.

That this is so was further established by the following experiment: a sample of pure *βl*-hydrindamine bromocamphorsulphonate was treated with concentrated hydrochloric acid, the precipitated hydrochloride separated, the filtrate evaporated several times with water, then diluted, and left for some hours; after separating the crystals of the *βl*-salt which had escaped decomposition, the solution, which contained the liberated bromocamphorsulphonic acid, was treated with *dl*-hydrindamine hydrochloride. The salt slowly deposited from this solution was free from the α-modification of the partially racemic salt, a fact which proved that the acid could not have been *ordinary* *d*-bromocamphorsulphonic acid; the salt consisted, in fact, of small, well-defined prisms, indistinguishable by inspection from those of the partially racemic β-salt and doubtless almost identical with those of the *synthetical* partially racemic β-salt recently described (Trans., 1903, **83**, 900).

The *d*-bromo-acid contained in the *βl*-hydrindamine salt and set free from it by hydrochloric acid is therefore different from the *d*-bromo-acid obtained from the same salt by first treating with baryta and then decomposing the barium salt with dilute sulphuric acid.

Now the possibility of the existence of isomeric *d*-bromocamphorsulphonic acids had been under consideration from the very commencement, and in the first paper on these isomeric salts this question was discussed at some length and many experiments were made in order to try and decide it (Trans., 1900, **77**, 877—882). The possibility of keto-enolic tautomerism in the group

$$\begin{matrix} -\mathrm{CHBr} \\ | \\ -\mathrm{CO} \end{matrix} \quad \rightleftarrows \quad \begin{matrix} -\mathrm{CBr} \\ \| \\ -\mathrm{C{\cdot}OH} \end{matrix},$$

was considered especially, examined experimentally, and rejected; that of the existence of stable isomeric acids, represented by the configurations

$$\begin{array}{c} \diagdown \\ \mathrm{H—C—Br} \\ | \\ \diagup\mathrm{C} \\ \| \\ \mathrm{O} \end{array} \quad \text{and} \quad \begin{array}{c} \diagdown \\ \mathrm{Br—C—H} \\ | \\ \diagup\mathrm{C} \\ \| \\ \mathrm{O} \end{array}$$

was also discussed and dismissed, partly from theoretical considerations based on the known behaviour of ordinary *cis-* and *trans-*modifications, but principally, no doubt, because the acid actually obtained from the α-salt was found to be identical with that prepared from the β-isomeride. The new facts just mentioned rendered it necessary, of course, to reconsider these possibilities, and it may now be taken as proved that the existence of structurally isomeric acids, convertible one into the other under particular conditions, but otherwise extremely stable, is the true explanation of the existence of the isomeric α- and β-salts. *d*-Bromocamphorsulphonic acid and the corresponding *d*-chloro-compound exist then in two stable forms; the acids contained in the β-salts may be named β- or *iso-d*-bromo- and β- or *iso-d*-chloro-camphorsulphonic acids respectively, the components of the α-salts being referred to as the α- or *normal* forms.*

These *iso*-acids and the normal forms are stable in aqueous solution, and in presence of hydrochloric acid even at 100°; they are also stable in neutral or acid solutions of their salts at 100°. In presence of free base, however, such as caustic potash, baryta, sodium carbonate, hydrindamine, &c., a small proportion of the normal acid is transformed into the *iso*-form, whereas under the same conditions the latter is almost entirely converted into the normal form. The condition of equilibrium seems to be attained when about 90—95 per cent. of the acid is present in the normal form; if, however, the salt of the β- or *iso*-form is evaporated with a solution of the free base, it is almost entirely transformed into the more sparingly soluble salt of the α- or normal acid.

The question next arises, what is the relationship between these isomeric forms of the sulphonic acids? In the author's opinion, neither of the isomerides represents the enolic modification, because neither the α- nor the β-hydrindamine salt gives a coloration with ferric chloride or interacts with phenylcarbimide (Trans., 1900, 77, 881). Also because α-bromocamphor, from which the bromo-sulphonic acid is derived, does not give a benzoyl derivative when shaken with benzoic chloride in alkaline solution; experiments recently made by the author

* The acids here named the β- or *iso*-acids for the sake of clearness should be indexed under the names $d\alpha'$-chloro- and $d\alpha'$-bromo-camphorsulphonic acid respectively, as they are α′- and not β-derivatives of camphor.

with the object of preparing such derivatives of α-bromocamphor and of camphor gave indubitably negative results. Further, because camphor-π-sulphonic acid and Reychler's camphorsulphonic acid,* both of which contain the group $-CH_2{\cdot}CO-$, and which, therefore, might theoretically exist in an enolic form, but which cannot yield *cis*- and *trans*-isomerides, do not give rise to isomeric hydrindamine salts (Trans., 1901, **79**, 370 and 437). It may be concluded, therefore, that the isomeric α- and β- or normal and *iso*-acids are the *cis*- and *trans*-forms, and that the conversion of one into the other in presence of bases takes place as indicated in the following formulæ:

$$C_8H_{13}(SO_3H)<\begin{matrix}C<\begin{matrix}H\\Br\end{matrix}\\|\\CO\end{matrix} \quad \longleftrightarrow \quad C_8H_{13}(SO_3H)<\begin{matrix}CBr\\\|\\C{\cdot}OH\end{matrix} \quad \longleftrightarrow$$

α- or normal acid. Unstable enolic form.

$$C_8H_{13}(SO_3H)<\begin{matrix}C<\begin{matrix}Br\\H\end{matrix}\\|\\CO\end{matrix}$$

β- or *iso*-acid.

During this transformation, the two compounds become *identical*, that is to say, they both pass through the same unstable enolic form.

A somewhat analogous case which has recently come under the author's observation may be quoted in support of this view. *d*-Methylhydrindone (Proc., 1902, **18**, 34) is apparently stable when pure, and is not changed by mineral acids, as is shown by the facts that its specific rotation does not alter appreciably in the course of several weeks, and the optically active ketone is actually prepared in presence of hydrogen chloride; consequently the ketone does not exist in the enolic form under these conditions. When, however, a trace of sodium ethoxide is added to its alcoholic solution, it rapidly and completely racemises, that is to say, it is doubtless converted into equal quantities of the *cis*- and *trans*-isomerides,

$$C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>C<\begin{matrix}H\\Me\end{matrix} \quad \longleftrightarrow \quad C_6H_4<\begin{matrix}CH_2\\C\\|\\OH\end{matrix}\geqslant CMe \quad \longleftrightarrow$$

d-Ketone. Enolic form.

$$C_6H_4<\begin{matrix}CH_2\\CO\end{matrix}>C<\begin{matrix}Me\\H\end{matrix}$$

l-Ketone.

* The fact that Reychler's camphorsulphonic acid does not give rise to isomeric hydrindamine salts may be taken as confirming the view that this acid is a β- and not an α-derivative of camphor (compare Armstrong and Lowry, Trans., 1902, **81**, 1473).

The discovery of the existence of the isomeric sulphonic acids and the above view as to their relationship account for all the facts observed in the study of the isomeric hydrindamine, benzylhydrindamine, methylhydrindamine, and *l*-menthylamine salts which are derived from them; the free acids, as ordinarily prepared, invariably consist of a mixture of the normal with a small proportion of the *iso*-form.

It may perhaps seem singular that it should have taken so long to arrive at what now appears to be such a simple and obvious explanation of the existence of these isomerides. The reason is, no doubt, that the truth was concealed or obscured by a combination of apparently disconnected facts, of which the following may be mentioned. Firstly, because the explanation originally suggested is, in one sense, so near the truth that it accounted for all the phenomena, excepting the observed values for the molecular rotations of the β-salts, just as well and in an even simpler manner than does the present one; the author's suggestion was that the isomeric salts contained respectively the groupings

$$\begin{array}{c} | \\ X{-}N{-}Y \\ / \backslash \end{array} \quad \text{and} \quad \begin{array}{c} | \\ Y{-}N{-}X \\ / \backslash \end{array};$$

the true explanation is that the isomeric forms are *cis*- and *trans*-modifications:

$$\begin{array}{c} | \\ X{-}C{-}Y \\ | \end{array} \quad \text{and} \quad \begin{array}{c} | \\ Y{-}C{-}X. \\ | \end{array}$$

Secondly, because of the production of apparently analogous isomerides from *cis*-π-camphanic acid, in which case the existence of such *cis*- and *trans*-forms seemed, and still seems, to be very improbable; the constitution assigned to this acid (Trans., 1896, **69**, 918) is not to be regarded as definitely established, but hitherto no indication of the existence of isomeric forms has been observed, and the nature of the isomeric salts to which it gives rise is still unknown.

Further, it must be borne in mind that no indication of the occurrence of intramolecular change has ever been obtained from an examination of the specific rotations of α-bromo- and α-chloro-camphor or of their sulphonic derivatives, whereas in the case of other α-derivatives of camphor, which are capable of existing in isomeric forms, such evidence is obtained at every turn and the one form passes into the other apparently spontaneously (compare Lowry, Trans., 1899, **75**, 211).

Also, it may be again noted, various experiments seemed to prove the non-existence of an enolic form of the bromo-acid (Trans., 1900, **77**, 881), and if this were so it seemed obvious that the ordinary acid could not be transformed into an *iso*-form and *vice versâ* under the

conditions employed by the author during the study of the isomeric salts; if, on the other hand, such a transformation were possible, then it seemed most probable that on crystallising any salt in the ordinary way only *one* form would be obtained, namely, the more sparingly soluble one, as is usual in such cases.

These and many other reasons, which are recorded in earlier papers, seemed of such weight as to render inadmissible the view that the salts were derived from *cis*- and *trans*-acids; the new facts prove the contrary. Nevertheless, all the old facts remain as recorded, and as regards the experimental part of the work there is, as far as the author knows, nothing to correct and nothing to withdraw.

Salts of the Normal and iso-*Forms of Bromo- and Chloro-camphorsulphonic Acids.*

The method invariably used for the preparation of these sulphonic acids is the decomposition of their barium salts with dilute sulphuric acid; the barium salts, which are prepared by boiling the ammonium salts with baryta, are formed in alkaline solution, and will therefore consist of the derivatives of both the normal and *iso*-acids. The acid prepared from this mixture of barium salts is therefore itself a mixture, as is also, doubtless, any salt obtained by neutralising the acid; this is clearly shown by the experiments on the "regeneration" of the salts of hydrindamine, methylhydrindamine, and menthylamine. It seems very probable, therefore, that the only pure salts of the normal acids which have so far been obtained are:

ad-Hydrindamine *d*-bromocamphorsulphonate,
al- ,, ,,
ad-Hydrindamine *d*-chlorocamphorsulphonate,
al- ,, ,,

and possibly the *ad*- and *al*-methylhydrindamine bromocamphorsulphonates and the salt of *l*-menthylamine.

Ordinary ammonium bromocamphorsulphonate certainly appears to be homogeneous, as its optical properties do not change when it is repeatedly crystallised (see above); whether this is due to the impossibility of separating the salt of the normal from that of the *iso*-acid or to the complete transformation of the *iso*- into the normal form during the evaporation of the ammoniacal solution is uncertain; the author inclines to the first view from a practical acquaintance with the extraordinary difficulty met with in separating the normal and *iso*-salts of hydrindamine and other organic bases, such as phenylethylamine (Hunter and Kipping, Trans., 1903, **83**, 1147). When, moreover, it is found that the partially racemic β-modification of hydrind-

amine bromocamphorsulphonate, which behaves like a homogeneous substance, is in reality a mixture of four very different salts,* it is quite credible that ammonium bromocamphorsulphonate and all other salts which have not been specially treated should contain a small proportion of the isomeric salt of the *iso*-acid.

Silver bromocamphorsulphonate, prepared from the acid, is probably also a mixture in spite of the fact that many organic salts, obtained by treating the silver salt with halogen derivatives of bases, were not resolved into appreciably different fractions after repeated crystallisation (Barrowcliff and Kipping, Trans., 1903, **88**, 1141).

As regards the salts of the β- or *iso*-acids, the only compounds hitherto obtained in a pure state are :

β*l*-Hydrindamine	*d*-bromocamphorsulphonate,	
β*d*-	,,	*d*-chlorocamphorsulphonate, and
β*l*-	,,	,,

The β-forms of *d*-hydrindamine *d*-bromocamphorsulphonate and of the corresponding salts obtained from *d*-methylhydrindamine, *l*-methylhydrindamine, and *l*-menthylamine were not obtained in a state of purity, as was indeed clearly recognised at the time (Tattersall and Kipping, Trans., 1903, **83**, 924; Tutin and Kipping, Trans., 1904, **85**, 65); that these salts should still contain such a very large proportion of the α-isomeride, as in fact they do (see p. 638), was, however, hardly to be expected.

Molecular Rotations of the Normal and iso-*Acids.*

Since it seems highly probable that most of the salts of α- or "normal" *d*-bromocamphorsulphonic acid contain a considerable quantity of the isomeric β-salt, it would follow that the value for the molecular rotation of the normal acid ion, as hitherto determined, is too low. The results obtained with the pure *d*- and *l*-hydrindamine salts give, as a mean value, $[M]_D$ +269°, which agrees well with that

* It seems very probable that the bromocamphorsulphonate of dihydro-α-methylindole, melting at 124—125°, obtained by Pope and Clarke (Trans., 1904, **85**, 1330) during their experiments on the resolution of the above-named base, is also a mixture of four compounds, namely :

d-Dihydro-α-methylindole			normal	*d*-bromocamphorsulphonate,	
l-	,,	,,	,,	,,	,,
d-	,,	,,	*iso*-	,,	,,
l-	,,	,,	,,	,,	,,

Its molecular rotation, $[M]_D$ +242·7° shows that it is not a salt of either the pure normal acid or of the pure *iso*-acid (compare p. 638), and the optical inactivity of the base obtained from it proves that its low molecular rotation is not due to excess of the *l*-base.

usually accepted ; such a value, however, based on determinations with two bases only can hardly be accepted as final and the true one is probably more nearly $[M]_D$ +280°.

The only pure salt of the β- or *iso*-bromo-acid which has been examined optically is the *l*-hydrindamine salt, which gives for the *iso*-acid ion the value $[M]_D$ +177° ; the molecular rotations of the "last fractions" of the *d*-methylhydrindamine, *l*-methylhydrindamine, and *l*-menthylamine salts, previously described, approximate to those of the normal rather than to those of the *iso*-acid, and it is obvious therefore that these "last fractions" contained a larger quantity of the normal than of the *iso*-acid.

The molecular rotations of the pure hydrindamine salts of normal chlorocamphorsulphonic acid give the value $[M]_D$ +185·5° for the normal acid ion, but the data are insufficient to give a reliable result ; in the case of the *iso*-acid, the examination of the same two hydrindamine salts gives $[M]_D$ +233° as the mean value for the *iso*-acid ion.

This is one of those cases which shows the extreme difficulty of establishing any definite connection between the constitution of a compound and its specific rotatory power ; it can hardly be doubted that the normal forms of the *d*-bromo- and *d*-chloro-acids correspond in configuration, and yet when the former is transformed into the *iso*-modification its molecular rotation falls by about 90°, whereas a corresponding intramolecular change in the chloro-acid increases the molecular rotation by about 48°. This curious fact assisted no doubt in concealing the true nature of the isomerism of the α- and β-salts.

The investigation of the *iso*-forms of *d*-bromo- and *d*-chloro-camphorsulphonic acids will be continued, but, as the only method at present available for their isolation is that of fractionally crystallising their salts with one of the optically active hydrindamines, it is obvious that they cannot be obtained very easily or in large quantities.

The further study of these sulphonic acids and of *d*-methylhydrindone may also help to elucidate the mechanism of tautomeric change, which, according to Lapworth and Hann (Trans., 1902, **81**, 1512), "may be the result of one or both of two superposed reactions, one due to ionisation in the compound itself, accelerated by bases and retarded by acids, and the other due to an additive phenomenon, accelerated by acids and retarded by bases."

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LXIV.—*Experiments on the Synthesis of the Terpenes. Part II. Synthesis of* Δ^3-p-*Menthenol*(8), $\Delta^{3.8(9)}$-p-*Menthadiene*, p-*Menthanol*(8), $\Delta^{8(9)}$-p-*Menthene, and* p-*Menthane*.*

By William Henry Perkin, jun., and Samuel Shrowder Pickles.

The first paper on this subject (Perkin, Trans., 1904, **85**, 654) dealt with the conversion of Δ^3-tetrahydro-*p*-toluic acid into terpineol, dipentene, and terpin, a series of changes which may conveniently be represented thus:

Δ^3-Tetrahydro-*p*-toluic acid, $Me{\cdot}C{<}{}^{CH-CH_2}_{CH_2{\cdot}CH_2}{>}CH{\cdot}CO_2H$.

Terpineol, $Me{\cdot}C{<}{}^{CH-CH_2}_{CH_2{\cdot}CH_2}{>}CH{\cdot}CMe_2{\cdot}OH$.

Dipentene, $Me{\cdot}C{<}{}^{CH-CH_2}_{CH_2{\cdot}CH_2}{>}CH{\cdot}C{<}{}^{CH_2}_{Me}$.

Terpin, $Me{\cdot}C(OH){<}{}^{CH_2{\cdot}CH_2}_{CH_2{\cdot}CH_2}{>}CH{\cdot}CMe_2{\cdot}OH$.

The present paper deals, in the first place, with some hitherto unknown members of the terpene series which have been synthesised by employing Δ^1-tetrahydro-*p*-toluic acid, instead of the Δ^3-tetrahydro-acid, in experiments similar to those which led to the syntheses just mentioned.

Δ^1-Tetrahydro-*p*-toluic acid, $Me{\cdot}CH{<}{}^{CH_2-CH}_{CH_2{\cdot}CH_2}{>}C{\cdot}CO_2H$,

has already been obtained by Einhorn and Willstätter (*Annalen*, 1894, **280**, 163) from α-bromohexahydro-*p*-toluic acid by treatment with quinoline. We prepared this acid in quantity by a modification of the above method (p. 645) and converted it into ethyl tetrahydro-*p*-toluate by the action of alcohol and sulphuric acid.

This ester reacts readily with an ethereal solution of magnesium methyl iodide yielding

Δ^3-*p*-menthenol(8), $Me{\cdot}CH{<}{}^{CH_2-CH}_{CH_2{\cdot}CH_2}{>}C{\cdot}CMe_2{\cdot}OH$,

* The system of nomenclature used in the papers of this series is that employed in the excellent account of the terpenes written for Meyer-Jacobson's *Lehrbuch* (Vol. II, i, pp. 876—962) by Prof. Carl Harries.

The basis of this system is hexahydrocymene and the numbering, in the case of the *p*-series,

(7)C–⟨1 2 3 4 5 6⟩–C(8)⟨C(9), C(10)⟩,

is that recommended by Baeyer (*Ber.*, 1894, **27**, 436).

which is isomeric with terpineol (Δ^1-*p*-menthenol-8) and differs, indeed, from this substance only in the position of the double linking in the ring, as a comparison of their formulæ will show.

It was therefore interesting to find that this new menthenol resembles terpineol, not only in odour, but also in many other properties.

Thus, when digested with potassium hydrogen sulphate, it is converted by loss of water into

$$\Delta^{3\cdot8(9)}\text{-}p\text{-menthadiene, } Me\cdot CH{<}{CH_2-CH \atop CH_2\cdot CH_2}{>}C\cdot C{<}{CH_2 \atop Me},$$

just as terpineol, under the same conditions, yields dipentene.

On the other hand, terpineol is a solid, crystalline substance, whereas Δ^3-*p*-menthenol(8) is liquid, and we have not been able to prepare from the latter a crystalline nitrosochloride or phenylurethane corresponding to these well known derivatives of terpineol. One of the most characteristic properties of terpineol is its conversion into terpin hydrate by the action of dilute sulphuric acid at the ordinary temperature,* but, although very careful experiments were made on the subject, there was no indication of any similar addition of water taking place when the new menthenol was subjected to exactly similar treatment. These differences in properties, due obviously to difference in the position of the double linking in the ring, are, perhaps, greater than might have been expected from so small a change in constitution. As stated above, Δ^3-*p*-menthenol(8), when digested with potassium hydrogen sulphate, yields $\Delta^{3\cdot8(9)}$-*p*-menthadiene, and the properties of this new hydrocarbon are very interesting, especially when compared with those of dipentene ($\Delta^{1\cdot8(9)}$-*p*-menthadiene), from which it differs only in the position of the double linking in the ring.

$\Delta^{3\cdot8(9)}$-*p*-Menthadiene distils at 186—187°, or a few degrees higher than dipentene (181°), and it possesses in an even more marked degree the odour of lemons so characteristic of the latter; apparently then this odour is not associated with any definite position of the double linking in the ring. In several other respects, however, the new terpene has properties which are very different from those of dipentene. The latter hydrocarbon yields a crystalline nitrosochloride, $C_{10}H_{16}$,NOCl, and hydrochloride, $C_{10}H_{16}$,2HCl, and is especially characterised by its behaviour towards bromine, with which it combines to form a crystal-

* In part I of this research (*loc. cit.*, p. 667), I ascribed to Tiemann and Schmidt (*Ber.*, 1895, **28**, 1781) the important discovery of the conversion of terpineol into terpin hydrate by the action of dilute sulphuric acid at the ordinary temperature. Prof. Wallach has kindly pointed out that the discovery was first made by Tilden (Trans., 1879, **35**, 289) and confirmed by himself (*Annalen*, 1885, **230**, 266) several years before the appearance of the paper by Tiemann and Schmidt.

—W. H. Perkin, jun.

line *tetra*bromide, $C_{10}H_{16}Br_4$. The new terpene reacts with nitrosochloride and with hydrogen chloride, yielding oily products which were not further investigated, but the most striking property which it exhibits is that it is capable of combining with only two atoms of bromine to form an unstable *di*bromide of the formula $C_{10}H_{16}Br_2$.

In this respect, then, the new terpene differs in a marked way from dipentene, and since both hydrocarbons are represented by formulæ containing two double linkings, this difference in behaviour appeared, at first, difficult to understand.

If, however, the formula of

$$\Delta^{3 \cdot 8(9)}\text{-}p\text{-menthadiene, } Me\cdot CH{<}\begin{matrix}CH_2-CH\\CH_2\cdot CH_2\end{matrix}{>}C\cdot C{<}\begin{matrix}CH_2\\Me\end{matrix},$$

is examined, it will be seen that the two double linkings are in the position –C⁚C·C⁚C–, and it has long been known that substances containing this grouping are only capable of uniting with two atoms of bromine to form derivatives in which that grouping becomes –CBr·C⁚C·CBr– (compare especially Baeyer and Herb, *Annalen*, 1890, **258**, 2; Thiele, *Annalen*, 1898, **306**, 87; 1901, **319**, 129). There can be no doubt that, in combining with two atoms of bromine, $\Delta^{3 \cdot 8(9)}$-*p*-menthadiene yields a dibromo-additive product of the formula

$$Me\cdot CH{<}\begin{matrix}CH_2\cdot CHBr\\CH_2-CH_2\end{matrix}{>}C{:}C{<}\begin{matrix}CH_2Br\\Me\end{matrix}$$

(3 : 9-dibromo-$\Delta^{4(8)}$-*p*-menthene), and that this substance is incapable of combining further with bromine without elimination of hydrogen bromide.

Similar results to the above were obtained in our experiments on the action of halogen acids on $\Delta^{3 \cdot 8(9)}$-*p*-menthadiene. It is well known that dipentene, $C_{10}H_{16}$, combines readily with *two* molecules of both hydrogen chloride and hydrogen bromide to yield the well characterised crystalline derivatives $C_{10}H_{16},2HCl$ and $C_{10}H_{16},2HBr$.

When $\Delta^{3 \cdot 8(9)}$-*p*-menthadiene is subjected to the action even of a very large excess of either of these reagents, it is only capable of combining with *one* molecule of each, yielding the liquid additive compounds $C_{10}H_{16},HCl$ and $C_{10}H_{16},HBr$.

Experiments which are in progress seem to indicate that all terpenes which contain the grouping –C⁚C·C⁚C– will be found to behave in a similar manner and to combine with only two atoms of bromine and one molecule of a halogen acid. The behaviour towards bromine and halogen acids may, therefore, in future prove to be of the highest importance in assigning a constitutional formula to a new terpene.

Included in the present paper are two other series of experiments, namely, the preparation of *p*-menthanol(8), $\Delta^{8(9)}$-p-menthene, and

p-menthane from ethyl hexahydro-*p*-toluate, and of *p*-tolyldimethylcarbinol and *p*-methyl*iso*propenylbenzene from ethyl *p*-toluate itself.

When ethyl hexahydro-*p*-toluate is allowed to react at the ordinary temperature with an ethereal solution of magnesium methyl iodide, it is converted into

$$p\text{-menthanol(8), Me}\cdot\text{CH}{<}{\begin{matrix}\text{CH}_2\cdot\text{CH}_2\\ \text{CH}_2\cdot\text{CH}_2\end{matrix}}{>}\text{CH}\cdot\text{CMe}_2\cdot\text{OH},$$

a crystalline substance which melts at 36°, distils at 207°, is volatile at the ordinary temperature, and has a penetrating odour of peppermint, properties which are almost identical with those of

$$\text{menthol } (p\text{-menthanol-3}), \text{ Me}\cdot\text{CH}{<}{\begin{matrix}\text{CH}_2\cdot\text{CH(OH)}\\ \text{CH}_2\text{——CH}_2\end{matrix}}{>}\text{CH}\cdot\text{CMe}_2\text{H},$$

from which it differs only in the position of the hydroxyl group. Besides menthol itself, three other menthanols are known, all of which contain the hydroxy-group in the ring, namely, tertiary carvomenthol(1), carvomenthol(2), and tertiary menthol(4), the numbers after the names indicating the position of the hydroxyl groups.

p-Menthanol(8) appears to be the first derivative of *p*-menthane, so far prepared, in which the hydroxy-group is situated in the *iso*propyl side chain. When *p*-menthanol(8) is heated with potassium hydrogen sulphate, it is decomposed with elimination of water and formation of

$$\Delta^{8(9)}\text{-}p\text{-menthene, Me}\cdot\text{CH}{<}{\begin{matrix}\text{CH}_2\cdot\text{CH}_2\\ \text{CH}_2\cdot\text{CH}_2\end{matrix}}{>}\text{CH}\cdot\text{C}{<}{\begin{matrix}\text{CH}_2\\ \text{Me}\end{matrix}},$$

a hydrocarbon which distils at 170° and has a faint odour resembling parsley and quite different from that of dipentene or $\Delta^{3.8(9)}$-*p*-menthadiene. This fact is interesting, because $\Delta^{8(9)}$-*p*-menthene is a dihydro-derivative of both these hydrocarbons, and in each case the formation of the dihydro-derivative has resulted in the disappearance of the double linking in the ring, and with this change in constitution the intense odour of lemons so characteristic of both has also disappeared. Besides the new hydrocarbon just described, only two of the six possible *p*-menthenes seem to have been prepared, namely, Δ^1-*p*-menthene (carvomenthene) and Δ^3-*p*-menthene. The latter may be readily obtained in quantity, as Zelinsky and Zelikoff (*Ber.*, 1901, **34**, 3253) have shown, by heating menthol with oxalic acid. It is very similar in properties to $\Delta^{8(9)}$-*p*-menthene, and like this substance has only a feeble odour. Both Δ^3-*p*-menthene and $\Delta^{8(9)}$-*p*-menthene are dihydro-derivatives of $\Delta^{3.8(9)}$-*p*-menthadiene; in the first case, the double linking in the side chain, and in the second that in the ring has been removed by the addition of two atoms of hydrogen. Since in both cases this change has resulted in the disappearance of the characteristic odour of lemons, it would seem to follow that this odour is dependent

n the presence both of the double linking in the ring and of that in the side chain.

$\Delta^{8(9)}$-*p*-Menthene is reduced with difficulty, even when dissolved in alcohol and treated with a large excess of sodium, but if its hydrobromide, $C_{10}H_{16},HBr$, is treated with zinc dust and acetic acid it is converted into

p-menthane (hexahydrocymene), $Me\cdot CH{<}{\substack{CH_2\cdot CH_2\\ CH_2\cdot CH_2}}{>}CH\cdot CMe_2H$.

This hydrocarbon had previously been obtained by several methods (see p. 652); it distils at 169—170° and has a rather feeble odour resembling that of light petroleum.

While considering the properties of the members of the terpene group which we had synthesised by the reactions mentioned above, some of which are derived from tetrahydro- and some from hexahydrobenzene, it occurred to us that it would be interesting to compare their properties with those of similarly constituted substances containing in the place of the reduced rings the benzene ring itself. We therefore treated ethyl *p*-toluate with magnesium methyl iodide and obtained a good yield of *p*-tolyldimethylcarbinol, $Me\cdot C_6H_4\cdot CMe_2\cdot OH$, a tertiary alcohol which had not previously been described.

This substance is a liquid which distils at 112° (16 mm.) and has a rather pleasant sweet odour, quite distinct from that of terpineol or any other similarly constituted alcohol belonging to the terpene group. When this alcohol is digested with potassium hydrogen sulphate, it is decomposed in the usual manner with elimination of water and formation of *p*-methyl*iso*propenylbenzene,

$$Me\cdot C_6H_4\cdot C{<}{\substack{CH_2\\ Me}},$$

a hydrocarbon of which dipentene and $\Delta^{3.8(9)}$-*p*-menthadiene are the tetrahydro-derivatives. It boils at 187° and possesses an odour very similar to that of cinnamene, and quite unlike that of a terpene; it combines with two atoms of bromine with formation of a liquid additive product, and yields a crystalline nitrosochloride which melts at 102°.

Reduction of p-*Toluic Acid.*

In preparing hexahydro-*p*-toluic acid, *p*-toluic acid, in quantities of 10 grams, was dissolved in *iso*amyl alcohol (500 c.c.) and reduced at the boiling temperature with sodium (50 grams), essentially according to the method recommended by Einhorn and Willstätter (*Annalen*, 1894, **280**, 160). The product was shaken with twice its volume of water, the aqueous solution separated from the *iso*amyl alcohol, nearly neutralised

with dilute sulphuric acid, and evaporated to a small bulk. After acidifying and extracting with ether in the usual way, the crude crystalline acid was dissolved in dilute sodium carbonate and oxidised with permanganate at 0° until the colour remained permanent, a stream of carbon dioxide being passed during the whole operation. By this means, the hexahydro-acid is freed from unsaturated acids (probably tetrahydro-*p*-toluic acids) which are always present. The filtrate from the manganese precipitate was evaporated, acidified, and extracted with ether, and the extract several times fractionated in order to separate the hexahydro-acid from considerable quantities of *iso*valeric acid. Lastly, the distilled acid was left in contact with porous porcelain until all oily impurity had been absorbed. Hexahydro-*p*-toluic acid melts at 112° and crystallises from formic acid in glistening prisms.

*Ethyl Hexahydro-*p*-toluate.*—In preparing this ester, the pure acid (38 grams) was dissolved in a cold mixture of ethyl alcohol (200 c.c.) and sulphuric acid (20 c.c.) and, after standing for two days, heated on the water-bath for one hour. Water was then added, the oily ester extracted with ether, the ethereal solution washed with water and dilute sodium carbonate, dried over calcium chloride, and evaporated. On distilling the residue, almost the whole quantity passed over at 207—208° (737 mm.) as a colourless oil having an unpleasant odour somewhat resembling that of amyl acetate.

0·2060 gave 0·5350 CO_2 and 0·1960 H_2O. C = 70·8; H = 10·7.
$C_{10}H_{18}O_2$ requires C = 70·6; H = 10·6 per cent.

The yield of ester was 32 grams, and the unchanged acid was readily recovered from the sodium carbonate washings by acidifying and extracting with ether.

*Bromination of Hexahydro-*p*-toluic Acid.*

According to Einhorn and Willstätter (*Annalen*, 1894, **280**, 161), hexahydro-*p*-toluic acid is not easily brominated by the Hell-Volhard process, and they therefore heated the acid first with phosphorus pentachloride and then with bromine in a sealed tube for three hours at 150°, or ten hours at 100°. The product was a black, tarry mass, from which, by repeated crystallisation, they were able to isolate pure *a*-bromohexahydro-*p*-toluic acid. As we required large quantities of the bromo-acid, and the employment of sealed tubes was very inconvenient, we re-investigated the matter, and found that, although the bromination takes rather longer than is usually the case with acids of this nature, it can be carried out almost quantitatively and without the formation of any tarry products if the following conditions are observed. Hexahydro-*p*-toluic acid (21 grams), contained in a flask

fitted with a ground-in condenser, is mixed with phosphorus pentachloride (42 grams), allowed to stand until the somewhat vigorous action has subsided, and then heated on the water-bath for about a quarter of an hour in order to complete the decomposition. Bromine (30 grams) is then added, and the heating continued for about two days and until the bromine has almost completely disappeared. The product is mixed with four times its volume of formic acid (sp. gr. 1·22), heated on the water-bath for half an hour, and then allowed to stand for 24 hours, when an almost colourless, crystalline cake of α-bromohexahydro-*p*-toluic acid will have separated. This is collected at the pump, drained on porous porcelain, and is then almost pure.

For reasons explained in the next section, we preferred in most of our experiments to employ ethyl α-bromohexahydro-*p*-toluate rather than the acid and this ester, which had not previously been described, we prepared in large quantities in the following manner. The oily product of the bromination of hexahydro-*p*-toluyl chloride, obtained as described above, was poured into excess of alcohol, and, after standing for some hours, water was added and the heavy oil extracted with ether. The ethereal solution was well washed with water and dilute sodium carbonate, dried over calcium chloride, evaporated, and the residue fractionated under reduced pressure, when ethyl α-bromohexahydro-*p*-toluate was obtained as a colourless oil which possessed a pungent and disagreeable odour, and distilled constantly at 144° (50 mm.). Owing, doubtless to some hydrogen bromide being eliminated during distillation, the analytical numbers obtained were somewhat lower than the theoretical.

0·2056 gave 0·1516 AgBr. Br = 31·1

$C_{10}H_{17}O_2Br$ requires Br = 32·1 per cent.

Δ¹-*Tetrahydro*-p-*toluic Acid.*

In our first experiments, this acid was prepared according to the directions given by Einhorn and Willstätter (*Annalen*, 1894, **280**, 163), namely, by heating α-bromohexahydro-*p*-toluic acid with quinoline, and purifying the resulting crude tetrahydro-acid by recrystallisation from dilute alcohol. We, however, subsequently found that the following process was much more convenient and gave a much better yield of the pure tetrahydro-acid. Powdered caustic potash (20 grams) is dissolved in hot methyl alcohol and, after cooling to about 40°, ethyl α-bromohexahydro-*p*-toluate (23 grams) is added; in a short time, the temperature rises to the boiling point and much potassium bromide separates. After heating on the water-bath for half an hour, the product is diluted with water, evaporated until free from alcohol, cooled and acidified, when tetrahydro-*p*-toluic acid separates in almost

colourless crystals. These were collected at the pump and purified by recrystallisation from formic acid or dilute acetic acid.

0·1698 gave 0·4266 CO_2 and 0·1296 H_2O. C = 68·5; H = 8·5.
$C_8H_{12}O_2$ requires C = 68·6; H = 8·6 per cent.

Δ^1-Tetrahydro-*p*-toluic acid crystallises in long, striated, prismatic needles, which melt at 134°; when heated under reduced pressure, the acid distils without decomposition.

Ethyl Δ^1-*Tetrahydro*-p-*toluate*, $C_7H_{11}\cdot CO_2Et$.—In preparing this ester, the tetrahydro-acid (43 grams) was added to a mixture of alcohol (200 c.c.) and sulphuric acid (20 c.c.) and the mixture warmed on the water-bath until the crystals had completely dissolved. After standing for two days and heating on the water-bath for half an hour, water was added and the oily ester extracted with ether. The ethereal solution was washed with water and dilute sodium carbonate, dried over calcium chloride and evaporated, and the residue purified by distillation, when almost the whole quantity passed over at 152—153° (100 mm.), the yield being nearly quantitative.

0·2194 gave 0·5746 CO_2 and 0·1902 H_2O. C = 71·4; H = 9·6.
$C_{10}H_{16}O_2$ requires C = 71·4; H = 9·5 per cent.

Ethyl Δ^1-*tetrahydro*-p-*toluate* is a colourless oil possessing a pungent odour somewhat resembling that of amyl acetate.

2-*Bromohexahydro*-p-*toluic Acid*.—Finely powdered tetrahydro-*p*-toluic acid dissolves readily in fuming hydrobromic acid (saturated at 0°) and the solution gradually deposits crystals of the above bromo-acid. After two days, these were collected and recrystallised from formic acid, from which the acid separates in glistening crystals.

0·2053 gave 0·1732 AgBr. Br = 35·9.
$C_8H_{13}O_2Br$ requires Br = 36·2 per cent.

2-*Bromohexahydro*-p-*toluic acid* is very readily soluble in alcohol, benzene, ether, or chloroform, but sparingly so in light petroleum. It crystallises well from dilute alcohol in microscopic needles.

1 : 2-*Dibromohexahydro*-p-*toluic Acid*, $C_7H_{11}Br_2\cdot CO_2H$.—The solution of tetrahydro-*p*-toluic acid in chloroform is only very slowly attacked by bromine, but, if the powdered acid is left exposed to dry bromine vapour, addition takes place readily and completely.

The product was exposed over caustic potash until the free bromine had been removed and then crystallised from formic acid.

0·2282 gave 0·2858 AgBr. Br = 53·3.
$C_8H_{12}O_2Br_2$ requires Br = 53·3 per cent.

1 : 2-*Dibromohexahydro*-p-*toluic acid* melts at 149°, but softens some-

what below this temperature; it is readily soluble in alcohol, ether, or benzene, but sparingly so in light petroleum. When the finely divided acid is shaken with sodium carbonate solution, it is converted into a sparingly soluble sodium salt which crystallises well from water but was not further investigated.

Δ^3-p-*Menthenol*(8).

The method employed in preparing this tertiary alcohol was as follows: dry magnesium powder (18 grams) * was suspended in pure dry ether (distilled first over sodium and then over phosphoric anhydride) in a large flask connected with a long, reflux condenser and then methyl iodide (100 grams) added in three portions, any violent ebullition being controlled by plunging the flask into running water. When the magnesium had dissolved, ethyl tetrahydro-*p*-toluate (40 grams) was poured in, when it was noticed that very little rise of temperature occurred during the first few minutes, but that the ether gradually became heated to its boiling point if care was not taken to keep the flask well cooled. After 12 hours, the product was cautiously decomposed by water and dilute hydrochloric acid, the ethereal solution separated, washed with water, evaporated, and digested with methyl-alcoholic potash (10 grams KOH) for 10 minutes on the water-bath, by which means any unchanged ester which might have been present was hydrolysed.

After diluting with water, the neutral oil was extracted with ether, the ethereal solution washed well, dried over calcium chloride and evaporated, and the residue distilled under reduced pressure (30 mm.). By far the larger portion passed over at 90—95° and consisted of almost pure $\Delta^{3 \cdot 8(9)}$-*p*-menthadiene (see the next section) and the remainder distilled at 110—135°. On refractioning the latter, an oil was obtained which distilled at 117—120° (25 mm.) and consisted of pure Δ^3-*p*-menthenol(8).

0·1412 gave 0·0431 CO_2 and 0·1498 H_2O. C = 77·8; H = 11·8.
$C_{10}H_{18}O$ requires C = 77·9; H = 11·7 per cent.

Δ^3-p-*Menthenol*(8) has a very penetrating and pleasant odour, which resembles and is even more pronounced than that of terpineol. Unlike the latter substance, it does not appear to yield a crystalline

* Later experiments on the conditions of formation of tertiary alcohols similar to Δ^3-*p*-menthenol(8) have shown that a much better yield is always obtained when the ester employed is treated with rather less than the calculated quantity of magnesium methyl iodide.

Any excess of the latter acts as a dehydrating agent, and this accounts for the formation of such large quantities of $\Delta^{3 \cdot 8(9)}$-*p*-menthadiene in the above experiment.

nitrosochloride or phenylurethane, at all events under the experimental conditions employed by us.

Since ordinary terpineol is readily converted into crystalline terpin hydrate when left in contact with dilute sulphuric acid, an experiment on the action of dilute sulphuric acid on Δ^3-*p*-menthenol(8) was carried out in the hope that a similar crystalline dihydroxy-compound might result, but this did not prove to be the case. After 10 grams of the pure menthenol had been shaken on the machine with 1 litre of 5 per cent. sulphuric acid for 10 days, almost the whole of the substance was recovered unchanged on extraction with ether.

$\Delta^{3.8(9)}$-p-*Menthadiene.*

This hydrocarbon is contained, together with some Δ^3-*p*-menthenol(8), in the fractions of the product of the action of magnesium methyl iodide on ethyl tetrahydro-*p*-toluate, which distilled at 90—95° (30 mm., see the previous section). In order to decompose the menthenol which was present, the oil (17 grams) was digested with powdered potassium hydrogen sulphate (25 grams) in a reflux apparatus for one hour. After distilling in steam, the distillate was extracted with ether, the ethereal solution dried over calcium chloride and evaporated, and the residual oil distilled, the portion passing over at 178—190° being collected separately. This oil was then twice fractionated and the fraction (185—188°) distilled three times over sodium and analysed:

0·1854 gave 0·5690 CO_2 and 0·1932 H_2O. C = 87·7; H = 11·6.

$C_{10}H_{16}$ requires C = 88·2; H = 11·8 per cent.

$\Delta^{3.8(9)}$-*p*-Menthadiene boils at 186—187° and possesses in a marked degree the intense odour of lemons so characteristic of dipentene; when cooled in liquid air, it solidifies to a glassy mass intersected with cracks, but the mass liquefies again at a temperature below − 40°. As the following experiment shows, it oxidises readily in the air, although apparently not so rapidly as dipentene. About 1 c.c. of the hydrocarbon was introduced into a tube standing over water, when it was found that in 6 days the water had risen 4·75 inches. Since the column of the original air was 24·5 inches in length, it follows that the absorption of the oxygen had been practically complete.

Action of Bromine.—$\Delta^{3.8(9)}$-*p*-Menthadiene is readily attacked by bromine, but, although it contains two double linkings, it is only capable of absorbing two atoms of bromine, as the following experiment shows (compare p. 641). The hydrocarbon (1·2 grams) was dissolved in chloroform (5 grams), the solution cooled to − 10°, and then bromine (diluted with twice its volume of chloroform) added slowly from a burette, every care being taken to keep the solution at − 10° during the whole operation. At first, the colour of the bromine disappeared

instantly, but as soon as the calculated quantity for the formula $C_{10}H_{16}Br_2$ had been added the colour was very slowly discharged and then only with evolution of hydrogen bromide. A second experiment led to exactly the same result. The product from the two experiments was freed from chloroform by aspirating a rapid current of dry air through it, and analysed, after leaving for two days in an exhausted desiccator over caustic potash and paraffin wax.

0·2010 gave 0·2526 AgBr. Br = 53·5.

$C_{10}H_{16}Br_2$ requires Br = 54·0 per cent.

This dibromide is readily acted on by zinc dust and acetic acid, but the reduction is a complicated one and we were unable to isolate any definite product.

Action of Hydrogen Chloride.—When freshly distilled $\Delta^{3.8(9)}$-*p*-menthadiene is dissolved in glacial acetic acid and saturated with hydrogen chloride at a temperature not exceeding 0°, it combines with the halogen acid to form the oily additive product, $C_{10}H_{16},HCl$.

After remaining for several hours, the solution was poured into ice water, rapidly extracted with ether, and the ethereal solution well washed with water and dilute sodium hydrogen carbonate. The bulk of the ether was then distilled off at as low a temperature as possible and the remainder removed over sulphuric acid in an exhausted desiccator. Unfortunately, although the experiment was repeated several times, the analysis always gave values which were considerably lower than those required by the formula $C_{10}H_{16},HCl$.

0·2902 gave 0·2178 AgCl. Cl = 18·7.

$C_{10}H_{17}Cl$ requires Cl = 20·5 per cent.

Very probably this additive compound is unstable and loses some hydrogen chloride during the necessary washing with water and dilute sodium hydrogen carbonate.

Action of Hydrogen Bromide.—In investigating the behaviour of $\Delta^{3.8(9)}$-*p*-menthadiene towards hydrogen bromide, the hydrocarbon, directly after distillation, was shaken in a stoppered bottle with six times its volume of fuming hydrobromic acid (saturated at 0°), the temperature, which is apt to rise considerably, being kept below 10° by cooling in ice water. After two hours, the product was poured into ice water, the heavy oil rapidly extracted with ether, the ethereal solution well washed with water, and the ether removed by careful evaporation and then over sulphuric acid in an exhausted desiccator. Two different preparations were analysed with the following results:

0·3807 gave 0·322 AgBr. Br = 36·0.

0·3041 gave 0·2584 AgBr. Br = 36·2.

$C_{10}H_{17}Br$ requires Br = 36·9 per cent.

$\Delta^{3.8(9)}$-p-*Menthadiene hydrobromide*, when prepared in this way, is a yellow oil which has an odour of oil of turpentine and is readily decomposed by boiling with water or dilute alkalis.

p-*Menthanol*(8).

This tertiary alcohol is produced when ethyl hexahydro-*p*-toluate reacts with magnesium methyl iodide.

Magnesium (8·4 grams) was suspended in dry ether and converted into magnesium methyl iodide in the usual way; the well-cooled solution was then mixed with ethyl hexahydro-*p*-toluate (30 grams), care being taken to prevent rise of temperature.

After standing overnight, the product was carefully decomposed with water and dilute hydrochloric acid, the ethereal solution washed, evaporated, and the residue digested with methyl-alcoholic potash (8 grams of KOH) for half an hour in order to remove any unchanged ester which might be present. After diluting with water, the oil was extracted with ether, the ethereal solution well washed, dried over calcium chloride, evaporated, and the oil fractionated under reduced pressure. Almost the whole quantity passed over at 99—101° (20 mm.) as a colourless oil which, on cooling, solidified in long, flat plates. The crystals were left in contact with porous porcelain until quite dry and then analysed:

0·1680 gave 0·4712 CO_2 and 0·1940 H_2O. C = 76·5; H = 12·8.

$C_{10}H_{20}O$ requires C = 76·9; H = 12·8 per cent.

p-*Menthanol*(8) melts at about 35—36° and is so soluble in the ordinary solvents that no attempt was made to recrystallise it; it distils at 206—207° (750 mm.) apparently without any decomposition, since the distillate solidifies at once on cooling. It volatilises rapidly at the ordinary temperature, and has a penetrating pleasant odour very similar to that of menthol, with which it is, of course, isomeric and closely allied in constitution.

$\Delta^{8(9)}$-p-*Menthene*.

This hydrocarbon is obtained when *p*-menthanol(8) is digested with anhydrous potassium hydrogen sulphate.

The pure alcohol (25 grams) was mixed in a reflux apparatus with powdered potassium hydrogen sulphate (40 grams) and heated to boiling for two hours in an oil-bath. Sufficient water was then added to dissolve the salt, the oil was extracted with ether, and, after very carefully drying over calcium chloride and evaporating, several times fractionated in order to remove a considerable quantity of unchanged *p*-menthanol(8) which was present. The fraction 169—172° was then

distilled three times over sodium, when almost the whole quantity passed over at 170—170·5° (746 mm.).

0·1340 gave 0·4287 CO_2 and 0·1619 H_2O. C = 87·2 ; H = 13·4.
0·1478 „ 0·4711 CO_2 „ 0·1758 H_2O. C = 86·9 ; H = 13·2.
$C_{10}H_{18}$ requires C = 87·0 ; H = 13·0 per cent.

$\Delta^{8(9)}$-p-*Menthene* has a peculiar odour, which at first resembles parsley but is afterwards reminiscent of lemons. It does not appear to oxidise in the air, and when dissolved in chloroform and cooled to − 10° it absorbs bromine without the evolution of hydrogen bromide. Several experiments were made in the hope of directly reducing $\Delta^{8(9)}$-*p*-menthene to *p*-menthane, but, although the hydrocarbon (7 grams) was treated in boiling alcoholic solution with 50 grams of sodium, only partial reduction took place, as the following analysis shows :

0·1132 gave 0·3581 CO_2 and 0·1395 H_2O. C = 86·3 ; H = 13·7.
p-Menthane, $C_{10}H_{20}$, requires C = 85·7 ; H = 14·3 per cent.

8-*Bromo*-p-*menthane*, $Me{\cdot}C_6H_{10}{\cdot}CBrMe_2$, *and* p-*Menthane*, $Me{\cdot}C_6H_{10}{\cdot}CHMe_2$.

When *p*-menthanol(8) is melted and then shaken in a tube with six times its volume of fuming hydrobromic acid (saturated at 0°), it appears at first to dissolve, but in a short time an oily layer separates on the surface of the hydrobromic acid. After one hour, the tube was sealed and heated at 50° for about 15 minutes, the contents of the tube being several times well shaken. Water was then added, the heavy oil extracted with ether, the ethereal solution well washed with water, dried over calcium chloride, and the ether removed by evaporation at as low a temperature as possible and finally over sulphuric acid in an exhausted desiccator.

0·3197 gave 0·276 AgBr. Br = 36·7.
$C_{10}H_{19}Br$ requires Br = 36·6 per cent.

8-*Bromo*-p-*menthane* is a colourless oil which has an odour somewhat resembling that of *iso*amyl bromide ; under 14 mm. pressure, it appears to distil without much decomposition at about 110°, but no analysis of the distilled product was made. In reducing this bromo-compound to *p*-menthane, the oil was dissolved in 10 vols. of glacial acetic acid and treated first in the cold and then at 50° with several small quantities of zinc dust, and after about half an hour the mass was heated on the water-bath with the addition of a few c.c. of a solution of hydrogen bromide in acetic acid. Water was then added, the oil extracted with ether, washed well with water, evaporated, and the reduction with zinc dust and acetic acid repeated twice exactly as

before. In order to be quite certain that the product was free from bromine, the oil (10 grams) was dissolved in alcohol (500 c.c.) and reduced at the boiling temperature with sodium (35 grams) in the usual way. After distilling in steam, the hydrocarbon was extracted with ether, twice distilled over sodium, and the fraction (169—170°) analysed:

0·1121 gave 0·3532 CO_2 and 0·1419 H_2O. C = 85·9; H = 14·0.
p-Menthane, $C_{10}H_{20}$, requires C = 85·7; H = 14·3 per cent.

The results of this analysis, and also the fact that the hydrocarbon reduced permanganate, showed clearly that the reduction had not been complete; the oil was therefore shaken on the machine with an excess of a 1 per cent. solution of potassium permanganate and a little caustic soda for 15 minutes, the hydrocarbon again extracted with ether and fractionated, when pure p-*menthane* was obtained distilling constantly at 169° (758 mm.).

0·1416 gave 0·4442 CO_2 and 0·1832 H_2O. C = 85·6; H = 14·4.

Berkenheim (*Ber.*, 1892, **25**, 688) found that *p*-menthane is produced when menthol is heated with hydriodic acid (sp. gr. 1·8) at 200°, and states that it boils at 169—170·5°. Shortly afterwards, Wagner (*Ber.*, 1894, **27**, 1638) showed that this hydrocarbon may be much more conveniently prepared by treating menthol with concentrated sulphuric acid at the ordinary temperature. The sulphuric acid acts, in this instance, as a reducing agent, and the *p*-menthane obtained distilled at 168—169°.

Jünger and Klages (*Ber.*, 1896, **29**, 317) also prepared *p*-menthane from menthyl chloride by reduction with sodium and alcohol, but they do not give the boiling point of the hydrocarbon which they obtained in this way. Lastly, Sabatier and Senderens (*Compt. rend.*, 1901, **132**, 566) showed that *p*-menthane is produced when the vapour of cymene, mixed with hydrogen, is passed over reduced nickel at 180°, and they give the boiling point as 166—168°.

p-*Tolyldimethylcarbinol.*

The ethyl *p*-toluate required for the preparation of the above substance was obtained by heating *p*-toluic acid (100 grams) with alcohol (400 c.c.) and sulphuric acid (40 c.c.) on the water-bath for four hours. After isolating in the usual way, 106 grams of pure ester were obtained boiling at 229—230°. This ester (33 grams) was now added to an ethereal solution of magnesium methyl iodide (containing 9 grams of magnesium), all rise of temperature being avoided by cooling in running water. After twelve hours, the product was decomposed by water and dilute hydrochloric acid and the ethereal solution washed

with water and evaporated. The oily residue was digested for half an hour with caustic potash (11 grams) dissolved in methyl alcohol, the neutral oil again precipitated by water and extracted with ether. The ethereal solution was well washed, dried over calcium chloride, evaporated, and the residual oil distilled under reduced pressure, when almost the whole quantity passed over at 111—112° (16 mm.).

0·2292 gave 0·6714 CO_2 and 0·1908 H_2O. C = 79·9 ; H = 9·3.
$C_{10}H_{14}O$ requires C = 80·0 ; H = 9·3 per cent.

p-*Tolyldimethylcarbinol* has a rather pleasant sweet odour quite distinct from that of terpineol. Cooled in liquid air, it solidified to a glassy mass cracked all through, and this again became almost liquid at −20°. When, however, the test-tube containing the substance was taken out of the liquid air and rubbed with a glass rod, the whole suddenly crystallised to an opaque solid at about −20°; this gradually melted, and the melting point registered by a thermometer placed in the melting liquid was seen to be about +5°.

p-*Tolyldimethylcarbinolphenylurethane*, $Me{\cdot}C_6H_4{\cdot}CMe_2{\cdot}O{\cdot}CO{\cdot}NH{\cdot}C_6H_5$.

In preparing this derivative, the alcohol (3 grams) was mixed with phenylcarbimide (2·5 grams) in a small flask fitted with an air condenser, and after heating on the water-bath for three hours the liquid was allowed to stand for three days. The contents of the flask, which had become almost solid, were left in contact with porous porcelain until quite dry, and the residue purified by recrystallisation from dilute methyl alcohol.

0·1402 gave 6·6 c.c. of nitrogen at 18° and 760 mm. N = 5·4.
$C_{17}H_{19}O_2N$ requires N = 5·2 per cent.

This phenylurethane crystallises from dilute methyl alcohol in small needles and melts at 119—120°.

p-*Methyl*iso*propenylbenzene*.

This hydrocarbon is readily prepared by acting on ethyl *p*-toluate with an excess of magnesium methyl iodide, when the latter acts as a dehydrating agent and converts a considerable quantity of the *p*-tolyldimethylcarbinol, first formed, into *p*-methyl*iso*propenylbenzene.

The quantities actually employed were: ethyl *p*-toluate (33 grams), magnesium (14 grams), and methyl iodide (85 grams).

The reaction was allowed to proceed without cooling, and the product was isolated in the manner described on the preceding page.

The oil thus obtained, which consists of a mixture of hydrocarbon

and alcohol, was digested for one hour with powdered potassium hydrogen sulphate in order to convert the alcohol into hydrocarbon, water was then added and the oil distilled in steam. The distillate was extracted with ether, the ethereal solution evaporated, and the residue fractionated, when almost the whole quantity passed over at 186—188° (780 mm.).

The hydrocarbon was then twice distilled over sodium and analysed:

0·1508 gave 0·5014 CO_2 and 0·1227 H_2O. C = 90·9; H = 9·1.
$C_{10}H_{12}$ requires C = 90·9; H = 9·1 per cent.

p-*Methyl*iso*propenylbenzene* distils constantly at 187° under 780 mm. pressure and possesses an odour similar to that of cinnamene, but at the same time, especially when hot, it has a slight odour of lemons. When cooled in liquid air, the hydrocarbon solidified in definite leaf-like crystals, and on removing the test-tube from the liquid air and allowing it to gradually melt a thermometer placed in the liquid indicated a melting point of approximately −20°.

p-Methyl*iso*propenylbenzene combines readily with two atoms of bromine, as the following experiment shows. The hydrocarbon (3·8 grams) was dissolved in two volumes of chloroform, cooled to −10°, and a solution of bromine in two volumes of chloroform added until the colour remained permanent, when it was found that 4·4 grams of bromine had been absorbed, whereas the formation of a dibromo-addition product requires the absorption of 4·6 grams of bromine.

The chloroform was removed by aspirating a current of dry air through the solution, the oily residue allowed to remain for two days over paraffin wax and solid caustic potash in an exhausted desiccator, and analysed.

0·3064 gave 0·3906 AgBr. Br = 54·3.
$C_{10}H_{12}Br_2$ requires Br = 54·7 per cent.

p-*Methyldibromo*iso*propenylbenzene* rapidly becomes yellow on exposure to light and air. When distilled under 15 mm. pressure, an oil passes over at 155—158°, which, however, contains only 45 per cent. of bromine, showing that some decomposition had taken place during the distillation.

The Nitrosochloride.—In preparing this derivative, the hydrocarbon (1 c.c.) was dissolved in methyl alcohol (1 c.c.), and after cooling to −10° mixed with *iso*amyl nitrite (1·5 c.c.). Concentrated hydrochloric acid (1·1 c.c.) and acetic acid (0·5 c.c.) were added drop by drop from a burette and the whole allowed to remain for one hour in the freezing mixture. When poured into ice water, an oil was precipitated, and when this had become almost solid it was left in contact with

porous porcelain until quite dry, rapidly washed at the pump with a little methyl alcohol, and then recrystallised from this solvent.

0·1708 gave 10·5 c.c. of nitrogen at 16° and 746 mm. N = 7·0.
$C_{10}H_{12}NOCl$ requires N = 7·1 per cent.

p-*Methyl*iso*propenylbenzene nitrosochloride* melts at 100—102° and is readily soluble in benzene or hot methyl alcohol, but sparingly so in light petroleum. It crystallises from a mixture of benzene and light petroleum in starry groups.

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LXV.—*Experiments on the Synthesis of the Terpenes. Part III. Synthesis of Aliphatic Compounds similar in constitution to Terpineol and Dipentene.*

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IT is often assumed, largely as the result of Baeyer's researches on the reduction of the phthalic acids, that, when derivatives of benzene are reduced, they not only lose their aromatic character, but at the same time acquire properties similar to those of open chain compounds of the aliphatic series. Since the terpenes are reduced benzene derivatives, it occurred to us that it would be interesting to attempt to prepare open chain compounds as closely allied as possible to the typical substances terpineol and dipentene in order to determine whether any great similarity in properties existed between such open chain compounds and these members of the terpene group. Our special object was to synthesise an alcohol which contained the double linking and the tertiary alcohol group $-CMe_2 \cdot OH$ in the same positions as in terpineol and which would, on elimination of water, yield a hydrocarbon in which the double linkings are situated as in dipentene.

In our first experiments, we subjected ethyl allylacetate to the action of magnesium methyl iodide and then heated the resulting tertiary alcohol in the usual manner with potassium hydrogen sulphate, by which means it was converted into the corresponding hydrocarbon.

If this series of reactions is represented thus :

Ethyl allylacetate, $CH_2{:}CH \cdot CH_2 \cdot CH_2 \cdot CO_2Et$,

Dimethylbutenylcarbinol, $CH_2{:}CH \cdot CH_2 \cdot CH_2 \cdot CMe_2 \cdot OH$,

*Allyl*iso*propenylmethane*, $CH_2{:}CH \cdot CH_2 \cdot CH_2 \cdot C{<}^{CH_2}_{Me}$,

and these formulæ compared with

$$\textit{Terpineol},\ Me\cdot C{<}^{CH-CH_2}_{CH_2\cdot CH_2}{>}CH\cdot CMe_2\cdot OH,$$

and

$$\textit{Dipentene},\ Me\cdot C{<}^{CH-CH_2}_{CH_2\cdot CH_2}{>}CH\cdot C{<}^{CH_2}_{Me},$$

it will be seen that the new open chain alcohol and hydrocarbon closely resemble terpineol and dipentene in structure.

Dimethylbutenylcarbinol is a liquid, the odour of which is undoubtedly somewhat similar to that of terpineol; it distils at 142·5° and yields a crystalline phenylurethane (m. p. 82°).

*Allyl*iso*propenylmethane* boils at 92°, and, like dipentene, readily absorbs oxygen from the air; it yields an oily tetrabromide and a crystalline nitrosochloride (m. p. 76°), but it has a very unpleasant acrid odour which is not in the least like that of dipentene.

In order to prepare compounds still more analogous in structure to terpineol and dipentene, we next submitted ethyl ethylallylacetate to the same series of reactions as we employed in the case of ethyl allylacetate. If the results obtained are represented as follows:

$$\textit{Ethyl ethylallylacetate},\ CH_2{\diagup}^{CH-CH_2}_{CH_3\cdot CH_2}{>}CH\cdot CO_2Et,$$

$$\textit{Dimethylethylisobutenylcarbinol},\ CH_2{\diagup}^{CH-CH_2}_{CH_3\cdot CH_2}{>}CH\cdot CMe_2\cdot OH,$$

$$\textit{Ethylallylisopropenylmethane},\ CH_2{\diagup}^{CH-CH_2}_{CH_3\cdot CH_2}{>}CH\cdot C{<}^{CH_2}_{Me},$$

the great similarity in constitution * between the two latter substances and terpineol and dipentene will at once be evident.

In investigating these substances, it was interesting to find that their properties approximate much more closely to those of terpineol and dipentene than is the case with the substances dimethylbutenylcarbinol and allyl*iso*propenylmethane.

Dimethylethylbutenylcarbinol boils at 165° and has a pronounced odour of terpineol and of peppermint; ethylallyl*iso*propenylmethane boils at 127° and has a pleasant odour of lemons and of peppermint, but the odour is different from that of dipentene.

The introduction of ethyl in the latter case has entirely removed the unpleasant acrid odour which characterised allyl*iso*propenyl-

* The similarity in structure between these open chain compounds, on the one hand, and Δ^3-normenthenol(8) and $\Delta^{3.8(9)}$-normenthadiene on the other (compare the following paper, p. 662) is perhaps still more striking, since the difference in the position of one of the double linkings is not likely to bring about much alteration in properties.

methane. Like dipentene, ethylallyl*iso*propenylmethane yields a tetrabromide, but, unlike the terpene, it does not appear to absorb oxygen from the air; this behaviour is curious, since, as has already been mentioned, allyl*iso*propenylmethane exhibits this property in a striking manner.

The results of this investigation indicate that open chain compounds analogous in structure to the terpenes and their derivatives, while showing certain similarities in behaviour, nevertheless possess properties different from those exhibited by the latter.

It appears, therefore, probable that the closed chain structure has a distinct influence on the properties of the terpenes and their derivatives.

Dimethylbutenylcarbinol, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe_2{\cdot}OH$.

In preparing this substance, pure ethyl allylacetate (30 grams) was added to an ethereal solution of magnesium methyl iodide containing 23 grams of magnesium. Very little action appeared to take place at first, but after a short time the ether commenced to boil and continued doing so for about fifteen minutes. After standing overnight, the product was decomposed by water and dilute hydrochloric acid, the ether separated, washed with a little sodium sulphite to remove iodine, evaporated, and the oily residue digested with methyl-alcoholic potash in order to hydrolyse the unchanged ester which might be present. The whole was diluted with water, extracted with ether, and, after washing well, drying over calcium chloride, and evaporating, the oil was purified by fractionation. In this way, 23 grams were obtained which distilled constantly at 142·5° and gave the following results on analysis:

0·1660 gave 0·4486 CO_2 and 0·1858 H_2O. C = 73·7; H = 12·4.
$C_7H_{14}O$ requires C = 73·7; H = 12·3 per cent.

Dimethylbutenylcarbinol is a colourless oil, possessing a very pronounced but not unpleasant odour, which is somewhat similar to that of terpineol; it is soluble in much water, but did not solidify when placed in a freezing mixture of ice and salt. An experiment on the action of dilute sulphuric acid on the alcohol was tried in the hope of obtaining the corresponding dihydric alcohol, but without success. The alcohol (6 grams) was mixed with 5 per cent. sulphuric acid (750 c.c.), shaken until completely dissolved, and then left at the ordinary temperature for four weeks. The solution was saturated with ammonium sulphate and extracted with ether, but the extract was found to consist almost entirely of the unchanged alcohol.

The *phenylurethane*, $C_7H_{13}O{\cdot}CO{\cdot}NH{\cdot}C_6H_5$, was prepared by heating the alcohol (3 grams) with phenylcarbimide (2·5 grams) for two hours

on the water-bath. The product, which solidified on cooling, was crystallised several times from methyl alcohol.

0·1762 gave 9 c.c. of nitrogen at 19° and 774 mm. N = 6·0.
$C_{14}H_{19}O_2N$ requires N = 6·0 per cent.

Dimethylbutenylcarbinol phenylurethane crystallises from methyl alcohol in prismatic needles and melts at 82°.

*Allyl*iso*propenylmethane*, $CH_2{:}CH{\cdot}CH_2{\cdot}CH_2{\cdot}CMe{:}CH_2$.

This hydrocarbon was prepared by boiling dimethylbutenylcarbinol (12 grams) with powdered potassium hydrogen sulphate (18 grams) for one hour in a reflux apparatus heated by means of an oil-bath.

The product was distilled and the distillate fractionated, when almost the whole quantity passed over at 90—96°, and after twice distilling over sodium the following analysis was made:

0·1126 gave 0·3615 CO_2 and 0·1274 H_2O. C = 87·5; H = 12·5.
C_7H_{12} requires C = 87·5; H = 12·5 per cent.

*Allyl*iso*propenylmethane* boils at 92°, has an acrid and very unpleasant odour, and decolorises bromine instantly in the cold.

In order to prepare the bromo-additive product, the hydrocarbon was diluted with an equal volume of chloroform, the solution cooled to − 10°, and then titrated with bromine until the colour ceased to be discharged, when it was observed that about the calculated quantity for the formation of a tetrabromide had been absorbed. By passing a rapid current of dry air through the product, the chloroform was removed, but at the same time some hydrogen bromide was eliminated and the analysis of the residue consequently gave numbers which were lower than the theoretical.

0·5306 gave 0·9566 AgBr. Br = 76·7.
$C_7H_{12}Br_4$ requires Br = 79·3 per cent.

*Allyl*iso*propenylmethane nitrosochloride*, C_7H_{12},NOCl.—This crystalline derivative is readily obtained by treating the solution of the hydrocarbon (3 c.c.) in methyl alcohol (3 c.c.) with *iso*amyl nitrite (4·5 c.c.) and, after cooling to − 10°, adding, drop by drop, concentrated hydrochloric acid (3·5 c.c.) and then acetic acid (0·5 c.c.), when crystals of the nitrosochloride soon begin to separate.

After remaining in the freezing mixture for an hour, the whole was poured on to ice, the crystals collected at the pump, drained on porous porcelain, and recrystallised from dilute methyl alcohol, when colourless needles were obtained which melted at 75—76° and consisted of the pure nitrosochloride.

0·1892 gave 0·1659 AgCl. Cl = 21·9.
$C_7H_{12}NOCl$ requires Cl = 21·9 per cent.

Allyl*iso*propenylmethane readily absorbs oxygen from the air, as was proved by the fact that a few drops placed in a burette over water had, in three days, absorbed almost 1/5th of the volume of air.

Dimethylethylbutenylcarbinol, $CH_2{:}CH{\cdot}CH_2{\cdot}CHEt{\cdot}CMe_2{\cdot}OH$.

The ethyl ethylallylacetate required for the synthesis of this alcohol had not previously been described. In order to obtain it, we prepared ethylallylmalonic acid in quantity from ethyl malonate by introducing first ethyl and then allyl in the usual way (compare Hjelt, *Ber.*, 1896, **29**, 1856), and heated the acid until evolution of carbon dioxide had ceased. The ethylallylacetic acid obtained by distilling the residue (143 grams from 250 grams of ethyl ethylmalonate) was dissolved in a three per cent. alcoholic solution of sulphuric acid (480 c.c.) and heated on the water-bath for five hours. Water was then added, the ester extracted with ether, the ethereal solution washed well with water and sodium carbonate, evaporated, and the residue fractionated, when *ethyl ethylallylacetate* was obtained as a colourless, unpleasant-smelling oil boiling at 166—167°.

0·1668 gave 0·4268 CO_2 and 0·1546 H_2O. C = 69·0; H = 10·2.
$C_9H_{16}O_2$ requires C = 69·2; H = 10·2 per cent.

The ester (31 grams) was added to a solution of magnesium methyl iodide (containing 19 grams of magnesium) and, after standing overnight, the product was cautiously decomposed by water and dilute sulphuric acid, the ethereal solution separated, washed with a little sodium hydrogen sulphite, and evaporated. The residue was then twice fractionated, when a colourless oil was obtained which distilled constantly at 165°.

0·1500 gave 0·4178 CO_2 and 0·1702 H_2O. C = 76·0; H = 12·7.
$C_9H_{18}O$ requires C = 76·0; H = 12·7 per cent.

Dimethylethylbutenylcarbinol has a very pronounced but pleasant odour of peppermint, which, at the same time, distinctly resembles that of terpineol. Unlike terpineol, however, it does not appear to be converted into a dihydric alcohol by long contact with dilute acids, as the following experiment shows. The alcohol (6 grams) was shaken with 5 per cent. sulphuric acid (800 c.c.) for four weeks, after which practically the whole was recovered unchanged by extraction with ether and fractionation under reduced pressure. We were also unsuccessful in our attempts to prepare a phenylurethane from the

alcohol by the action of phenylcarbimide, as this substance acted simply as a dehydrating agent and diphenylcarbamide was the only crystalline substance formed.

*Ethylallyl*iso*propenylmethane*, $CH_2{:}CH{\cdot}CH_2{\cdot}CHEt{\cdot}CMe{:}CH_2$.

In preparing this hydrocarbon, dimethylethylbutenylcarbinol (13 grams) was digested with powdered potassium hydrogen sulphate (20 grams) for two hours in a reflux apparatus heated in an oil-bath. Sufficient water was then added to dissolve the sulphate, the oil extracted with ether, the ethereal solution dried over calcium chloride, evaporated, and the hydrocarbon fractionated, first alone and then twice over sodium.

0·1858 gave 0·5880 CO_2 and 0·2184 H_2O. C = 86·3; H = 13·0.
0·1672 gave 0·5315 CO_2 and 0·1966 H_2O. C = 86·7; H = 13·0.
C_9H_{16} requires C = 87·1; H = 12·9 per cent.

*Ethylallyl*iso*propenylmethane* boils at 127° (740 mm.) and has a strong odour of peppermint and at the same time of lemons, the odour being entirely different from the unpleasant odour of allyl*iso*propenylmethane. It differs also from the latter hydrocarbon in that it does not appear to oxidise in the air. This remarkable difference was evident from parallel experiments made in burettes over water when no absorption could be observed in the case of ethylallyl*iso*propenylmethane, whereas the allyl*iso*propenylmethane had, in three days, absorbed almost the whole of the oxygen from the volume of air taken. Ethylallyl*iso*propenylmethane instantly decolorises bromine in the cold and, in an experiment with three grams of the hydrocarbon carried out under the conditions described on p. 658, the amount of bromine absorbed was almost exactly that required for the formation of a tetrabromide. After removing the chloroform by a rapid current of dry air, the residue was left in an exhausted desiccator over caustic potash and paraffin wax for two days and then analysed.

0·2949 gave 0·4762 AgBr. Br = 68·7
$C_9H_{16}Br_4$ requires Br = 72·0 per cent.

The reason for the figures being lower than those required by theory is that on standing in the desiccator the oil, which was originally almost colourless, had become brown and some hydrogen bromide was eliminated at the same time.

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LXVI.—*Experiments on the Synthesis of the Terpenes. Part IV. Synthesis of* Δ^3-*Normenthenol*(8), $\Delta^{3\cdot8(9)}$-*Normenthadiene, Normenthanol*(8), $\Delta^{8(9)}$-*Normenthene, &c.**

By KŌICHI MATSUBARA and WILLIAM HENRY PERKIN, jun.

BY far the greater number of the terpenes and their derivatives which have been extracted from the various essential oils have been found to be closely related to cymene or *p*-methyl*iso*propylbenzene, and it is remarkable that Nature should so persistently select that hydrocarbon as the foundation on which to build up the great variety of these products of the vegetable kingdom.

In considering this point it seemed to us that it would be interesting, for the sake of comparison, not only to synthesise terpenes derived from *o*- and *m*-methyl*iso*propylbenzenes, but also to investigate the properties of similarly constituted substances containing only the *iso*propyl group attached to the reduced benzene ring. The latter part of this investigation is now complete and, in the present paper, we give an account of a series of substances closely related to those described in Part II of this research, but differing from them in that they do not contain the methyl group. The starting point in these experiments was hexahydrobenzoic acid,

$$CH_2<{CH_2\cdot CH_2 \atop CH_2\cdot CH_2}>CH\cdot CO_2H,$$

which was prepared by a modification of Markownikoff's method (*Ber.*, 1892, 25, 3357), namely, from benzoic acid by reduction with sodium in *iso*amyl-alcoholic solution.

When this acid is treated with phosphorus pentachloride and then with bromine and the product poured into alcohol, a good yield of ethyl α-bromohexahydrobenzoate,

$$CH_2<{CH_2\cdot CH_2 \atop CH_2\cdot CH_2}>CBr\cdot CO_2Et,$$

* In naming these new substances, it has been thought best, for the sake of continuity, to employ the same system of nomenclature as in the other papers of this series, and the prefix "nor" has been adopted in order to indicate the absence of the methyl group.

Furthermore, in order to avoid complications which otherwise might easily arise, the same scheme of numbering is employed as before, that is:

$$\text{(ring 1–6)}-C^{(8)}<{C^{(9)} \atop C^{(10)}}$$

(compare p. 639), the position 7 being necessarily omitted.

is obtained and this bromo-ester is then readily decomposed by boiling with diethylaniline with elimination of hydrogen bromide and formation of ethyl Δ^1-tetrahydrobenzoate,

$$CH_2{<}{CH_2-CH \atop CH_2\cdot CH_2}{>}C\cdot CO_2Et.$$

This ester reacts readily with an ethereal solution of magnesium methyl iodide and is converted into Δ^3-normenthenol(8),

$$CH_2{<}{CH_2-CH \atop CH_2\cdot CH_2}{>}C\cdot CMe_2\cdot OH,$$

a substance which distils at 96—97° (25 mm.) and has properties very similar to those of Δ^3-*p*-menthenol(8), from which it differs only in the absence of the *p*-methyl group (compare this vol., p. 647).

When Δ^3-normenthenol(8) is mixed with an ethereal solution of magnesium methyl iodide, the latter acts as a dehydrating agent and converts the alcohol into $\Delta^{3\cdot 8(9)}$-normenthadiene,

$$CH_2{<}{CH_2-CH \atop CH_2\cdot CH_2}{>}C\cdot C{<}{CH_2 \atop Me},$$

a hydrocarbon which distils at 162°, readily absorbs oxygen from the air, and possesses in a marked degree the odour of lemons so characteristic of dipentene and $\Delta^{3\cdot 8(9)}$-*p*-menthadiene. This latter property seems to point to the fact that the odour of lemons, while somewhat modified by, is not dependent on, the presence of the *p*-methyl group. $\Delta^{3\cdot 8(9)}$-Normenthadiene is also similar to $\Delta^{3\cdot 8(9)}$-*p*-menthadiene in this respect, that it is only capable of combining with two atoms of bromine to yield a dibromide which, doubtless, has the constitution

$$CH_2{<}{CH_2\cdot CHBr \atop CH_2-CH_2}{>}C{:}C{<}{CH_2Br \atop Me},$$

and this peculiarity is due in both cases to the presence in the hydrocarbons of the grouping $-C{:}C\cdot C{:}C-$, an interesting point which has been discussed in a previous paper (this vol., p. 641).

A curious result was obtained in attempting to prepare $\Delta^{3\cdot 8(9)}$-normenthadiene by the action of powdered potassium hydrogen sulphate on Δ^3-normenthenol(8) under the usual conditions as, although some of this hydrocarbon was obtained in this way, the principal product was a hydrocarbon, $C_{18}H_{28}$, which distils at 172° (16 mm.), and is obviously a condensation product of two molecules of normenthadiene; for this reason, we have named it dinormenthadiene (p. 668).

This substance is probably similar in structure to the diterpenes, $C_{20}H_{32}$, which have been isolated from copaiva balsam and distil at about 250°, but which, so far, have been little investigated.

Proceeding with this investigation on the lines followed in Part II

of this series, we next prepared ethyl hexahydrobenzoate and submitted this to the action of magnesium methyl iodide, with the result that we obtained normenthanol(8),

$$CH_2{<}{CH_2{\cdot}CH_2 \atop CH_2{\cdot}CH_2}{>}CH{\cdot}CMe_2{\cdot}OH,$$

as a colourless syrup which distils at 196°, yields a phenylurethane melting at 87°, and has an odour very similar to that of menthol.

When this alcohol is digested with potassium hydrogen sulphate, it behaves normally and is converted, with loss of water, into $\Delta^{8(9)}$-normenthene,

$$CH_2{<}{CH_2{\cdot}CH_2 \atop CH_2{\cdot}CH_2}{>}CH{\cdot}C{\ll}{CH_2 \atop Me},$$

which distils at 158°, has a rather faint odour somewhat resembling that of parsley, does not absorb oxygen from the air, and decolorises bromine with the formation of a dibromide. It will thus be seen that $\Delta^{8(9)}$-normenthene has properties very similar to those of $\Delta^{8(9)}$-*p*-menthene (this vol., p. 650).

We next investigated the behaviour of normenthanol(8) on treatment with hydrobromic acid and found that reaction takes place readily with the formation of 8-*bromonormenthane*,

$$CH_2{<}{CH_2{\cdot}CH_2 \atop CH_2{\cdot}CH_2}{>}CH{\cdot}CBrMe_2,$$

which distils, with little decomposition, at 105° (25 mm.) and, when reduced with zinc dust and acetic acid, is converted into *normenthane* or *iso*propylhexamethylene,

$$CH_2{<}{CH_2{\cdot}CH_2 \atop CH_2{\cdot}CH_2}{>}CH{\cdot}CHMe_2,$$

an oil boiling at 150—153°, which possesses an odour very similar to that of light petroleum.

Lastly, in order that we might compare their properties with those of the reduced benzene derivatives described in this paper, we prepared phenyldimethylcarbinol, $C_6H_5{\cdot}CMe_2{\cdot}OH$ (m. p. 35°), and *iso*propenylbenzene, $C_6H_5{\cdot}CMe{:}CH_2$ (b. p. 164°), by a new process, namely, from ethyl benzoate by treatment with magnesium methyl iodide and subsequent elimination of water in the usual manner. These substances had already been obtained in another way, and a description of their properties will be found on pp. 671 and 672.

Hexahydrobenzoic acid, $C_6H_{11}{\cdot}CO_2H$, *and its Ethyl Ester*, $C_6H_{11}{\cdot}CO_2Et$.

Hexahydrobenzoic acid was first prepared by Aschan (*Ber.*, 1891, **24**, 1864 and 2617) from β-bromohexahydrobenzoic acid by reduction

with zinc dust and acetic acid; it was subsequently obtained synthetically, in small quantities, by the action of pentamethylene dibromide, $Br(CH_2)_5Br$, on the sodium derivative of ethyl malonate (Haworth and Perkin, Trans., 1894, **65**, 103), and Markownikoff (*Ber.*, 1892, **25**, 3357) showed that it may be prepared by pouring a solution of benzoic acid in capryl alcohol (or *iso*amyl alcohol) on to melted sodium. As these processes were all inconvenient for the preparation of the considerable quantities of this acid which we required for this research, we worked out the following method of preparation, which is similar to that employed in the reduction of *p*-toluic acid (this vol., p. 643), and which allows of large quantities of the pure acid being prepared with much less labour than hitherto. Benzoic acid (20 grams) is dissolved in one litre of *iso*amyl alcohol and, after heating to boiling in a large flask connected with a wide reflux condenser, sodium (100 grams) is added in two portions. As soon as the sodium has dissolved, the mass is shaken with water (2 vols.), the aqueous solution separated, and the *iso*amyl alcohol distilled until the temperature rises to 130°, when it is ready for a subsequent reduction. The aqueous extracts from several such operations were evaporated on the water-bath until the odour of *iso*amyl alcohol had disappeared, acidified with dilute sulphuric acid, and extracted with ether; the ethereal solution was then washed with water, dried over calcium chloride, evaporated, and the residue distilled.

The distillate, which consists of hexahydrobenzoic acid mixed with varying quantities of tetrahydrobenzoic acid and *iso*valeric acid, is dissolved in dilute sodium carbonate, mixed with powdered ice, and then a cold saturated solution of permanganate run in until the colour just remains permanent, the liquid being well stirred with a turbine, and a stream of carbon dioxide being passed during the whole operation. After removing any excess of permanganate by sodium sulphite, the product is heated to boiling and the filtrate and washings of the manganese precipitate evaporated nearly to dryness, acidified, and distilled in steam. The distillate is saturated with salt, extracted twice with ether, the ethereal solution washed with water, dried over calcium chloride, evaporated, and carefully fractionated in order to remove the considerable quantities of *iso*valeric acid which are always present. In this way, pure hexahydrobenzoic acid is obtained as a colourless oil distilling at 229—232°, and which solidifies, on cooling, to a crystalline mass which melts at 28°.

Ethyl Hexahydrobenzoate.—In preparing this ester, the pure acid (60 grams) was mixed with a cold solution of sulphuric acid (24 c.c.) in absolute alcohol (240 c.c.) and, after standing overnight, the mixture was heated for one hour on the water-bath. Water was then added, the ester extracted with ether, the ethereal solution washed

with water and sodium carbonate, dried over calcium chloride, evaporated, and the residue distilled.

0·115 gave 0·2918 CO_2 and 0·1057 H_2O. C = 69·1 ; H = 10·2.
$C_9H_{16}O_2$ requires C = 69·2 ; H = 10·2 per cent.

Ethyl hexahydrobenzoate is a colourless oil which distils at 193—195° and has an odour resembling that of the esters of the higher fatty acids. Aschan (*Annalen*, 1892, **271**, 264), who first prepared this ester, gives the boiling point as 194·5—195·5°.

Ethyl Tetrahydrobenzoate, $C_6H_9\cdot CO_2Et$.

After several experiments, the following process was adopted for the preparation of this ester. Hexahydrobenzoic acid (20 grams) is mixed with phosphorus pentachloride (35 grams) in a flask fitted with a ground-in condenser and, after the reaction has subsided, the decomposition is completed by heating on the water-bath for fifteen minutes. The solution of the acid chloride in phosphorus oxychloride is cooled, mixed with bromine (10 c.c.), and then heated on the water-bath until nearly all the bromine has disappeared, an operation which requires 12—15 hours. The product is then cooled and poured, in a thin stream, into absolute alcohol (300 c.c.), the violent reaction being controlled by running water. After standing overnight, water is added, the brown oily layer extracted with ether, the ethereal solution washed with sodium sulphite to remove excess of bromine, then with sodium carbonate, dried over calcium chloride, evaporated, and the residue fractionated under reduced pressure.

The greater portion distilled at 125—127° (25 mm.), but the numbers obtained on analysis were always too low, owing, apparently, to some hydrogen bromide being eliminated during distillation.

0·2655 gave 0·1999 AgBr. Br = 32·1.
$C_9H_{15}O_2Br$ requires Br = 34·0 per cent.

Ethyl α-bromohexahydrobenzoate is a heavy oil which possesses in a marked degree the penetrating, unpleasant smell characteristic of the esters of the α-bromo-fatty acids.

The conversion of this bromo-ester into ethyl Δ^1-tetrahydrobenzoate was carried out as follows. The bromo-ester (15 grams) was mixed with diethylaniline (25 grams) and, after heating in an oil-bath at 180° for one hour, the product was poured into dilute sulphuric acid and extracted with ether. The ethereal solution was well washed with dilute sulphuric acid, then with dilute sodium carbonate, dried over calcium chloride and evaporated, and the residue purified by fractionation under reduced pressure. By far the larger portion distilled at

143—145° (100 mm.) and a specimen boiling constantly at 143° was collected separately for analysis.

0·2443 gave 0·6257 CO_2 and 0·2038 H_2O. C = 69·8; H = 9·3.
0·2857 ,, 0·7285 CO_2 and 0·2327 H_2O. C = 69·6; H = 9·1.
$C_9H_{14}O_2$ requires C = 70·1; H = 9·1 per cent.

Ethyl Δ^1-tetrahydrobenzoate is a colourless oil possessing a pungent odour somewhat resembling that of hyacinths.

Δ^3-*Normenthenol*(8), $C_6H_9 \cdot CMe_2 \cdot OH$.

This substance is readily obtained when ethyl Δ^1-tetrahydrobenzoate (10 grams) is added to an ethereal solution of magnesium methyl iodide (containing 5 grams of magnesium), care being taken to avoid all rise of temperature. After standing overnight, the product was decomposed by water and dilute sulphuric acid, the ethereal solution separated, washed with dilute sulphuric acid and with water, dried over calcium chloride, and evaporated. On distilling the residue under 25 mm. pressure, almost the whole quantity passed over at 95—100°, and after a second fractionation the boiling point was constant at 96—97°.

0·1153 gave 0·3268 CO_2 and 0·1173 H_2O. C = 77·3; H = 11·3.
$C_9H_{16}O$ requires C = 77·1; H = 11·4 per cent.

Δ^3-*Normenthenol*(8) has an odour like that of cymene and peppermint. When cooled in liquid air, it solidified to a glass filled with cracks but, on removing from the liquid air, it became syrupy again at about −40°. Distilled under the ordinary pressure, it decomposes in a curious manner; at first a good deal of water is given off, then, if the operation is rapidly conducted, about half distils at 195—197°, the distillate having an unpleasant acrid odour like that of burning fat. A considerable amount of a less volatile residue remains in the flask and appears to consist of dinormenthadiene (compare p. 668).

$\Delta^{3.8(9)}$-*Normenthadiene*, $C_6H_9 \cdot CMe{:}CH_2$.

This hydrocarbon is formed when Δ^3-normenthenol(8) is digested with potassium hydrogen sulphate but, owing to the formation of dinormenthadiene and other condensation products, the yield obtained is sometimes very small. The best method of preparing it is to treat ethyl Δ^1-tetrahydrobenzoate with a large excess of magnesium methyl iodide, when the excess of the latter acts as a dehydrating agent on the Δ^3-normenthenol(8) which is first formed.

Ethyl Δ^1-tetrahydrobenzoate (1 mol.) was added to an ethereal solution of magnesium methyl iodide (4 mols.) and the reaction

allowed to proceed without cooling. After 24 hours, the product was treated with water and dilute sulphuric acid, the ethereal solution separated, dried over calcium chloride, evaporated, and the residue fractionated under the ordinary pressure. Almost the whole quantity distilled at 160—170°, and after this had been again carefully fractionated, the oil which passed over at 159—162° was three times distilled over sodium.

0·1602 gave 0·5198 CO_2 and 0·1632 H_2O. C = 88·5 ; H = 11·3.
C_9H_{14} requires C = 88·5 ; H = 11·5 per cent.

$\Delta^{3.8(9)}$-*Normenthadiene* distils at 161—162° (760 mm.) and has a strong odour of lemons and oil of turpentine which resembles, and yet differs from, that of dipentene. It oxidises rapidly in the air, as was shown by the fact that a small quantity confined in a burette over water had, in four days, absorbed nearly one-fifth of the volume of air taken. When cooled in liquid air, it solidifies to a glass which liquefies again at a very low temperature. The behaviour of this hydrocarbon towards bromine was very carefully investigated, and it was found that although it contains two double linkings, it is, nevertheless, only capable of absorbing two atoms of bromine, its behaviour in this respect being exactly similar to that of $\Delta^{3.8(9)}$-*p*-menthadiene (p. 648). The hydrocarbon (2·04 grams) was dissolved in three times its volume of chloroform, cooled to − 10°, and then a standard solution of bromine in chloroform was added, any rise of temperature being carefully avoided. The colour disappeared at first instantly, but when 2·2 grams of bromine had been added, traces of hydrogen bromide were observed, and after 2·4 grams had been run in, the colour was discharged only very slowly and then with copious evolution of hydrogen bromide. For the formation of a dibromide, the amount of hydrocarbon taken should have decolorised 2·67 grams of bromine, so that it is obvious that normenthadiene is only capable of yielding a dibromide by the direct addition of bromine. The product obtained in the above experiment after 2·45 grams of bromine had been added was freed from chloroform by passing a rapid current of dry air, and the residue allowed to remain for two days over caustic potash and paraffin wax in an exhausted desiccator. The analysis then gave numbers agreeing approximately with those required for the dibromo-additive product of the hydrocarbon.

0·2894 gave 0·3908 AgBr. Br = 57·5
$C_9H_{14}Br_2$ requires Br = 56·7 per cent.

The constitution of this dibromide is discussed on p. 662.

Dinormenthadiene, $C_{18}H_{28}$.

In our first attempts to prepare $\Delta^{3.8(9)}$-normenthadiene, a quantity of Δ^3-normenthenol(8) was digested with potassium hydrogen sulphate in the usual way. On submitting the product to distillation in steam, we were surprised to find that only a very small quantity of oil passed over readily, the remainder being volatile only with great difficulty. From the steam distillate, a small quantity of $\Delta^{3.8(9)}$-normenthadiene only was obtained, a good deal of a less volatile oil being present. This latter was mixed with the ethereal extract of the steam distillation flask and submitted to careful fractionation. In this way, a considerable quantity of a pale yellow oil was obtained which distilled constantly at 170—172° (16 mm.), but a large amount of a less volatile residue was left. The analysis of the oil distilling at 170—172° (16 mm.) gave the following results:

0·2080 gave 0·6754 CO_2 and 0·2102 H_2O. C = 88·5; H = 11·3.
0·2498 ,, 0·8060 CO_2 ,, 0·2517 H_2O. C = 88·0; H = 11·2.
$C_{18}H_{28}$ requires C = 88·5; H = 11·5 per cent.

A determination of the molecular weight of this substance by the cryoscopic method, using benzene as the solvent, gave 246 and 227, whereas the molecular weight of $C_{18}H_{28}$ is 244. There can therefore be no doubt that this substance is *dinormenthadiene*, produced by the condensation of two molecules of $\Delta^{3.8(9)}$-normenthadiene. When the solution of this substance in dry ether is saturated with hydrogen chloride, it becomes first yellow, then brown, and lastly an intense violet, but no crystals of a hydrochloride separate.

Normenthanol(8), $C_6H_{11}\cdot CMe_2\cdot OH$.

This tertiary alcohol is readily obtained by the action of magnesium methyl iodide on ethyl hexahydrobenzoate (p. 665).

Magnesium (6·7 grams) suspended in ether was converted into magnesium methyl iodide in the usual way and then ethyl hexahydrobenzoate (21·7 grams) added, all rise of temperature being carefully avoided. After remaining overnight in running water, the product was decomposed with water and dilute hydrochloric acid in the usual manner; the ethereal solution was then separated and evaporated. In order to decompose unchanged ethyl hexahydrobenzoate which was found to be present, the oil was digested for half an hour with 7 grams of caustic potash (dissolved in methyl alcohol), water was then added, and the oil again extracted. The ethereal solution after being well washed with water and dried over calcium chloride, deposited, on

evaporation, an oil which, after two fractionations under 25 mm. pressure, distilled constantly at 100—102°.

0·2002 gave 0·5575 CO_2 and 0·2265 H_2O. C = 75·9; H = 12·6.
$C_9H_{18}O$ requires C = 76·0; H = 12·7 per cent.

Normenthanol(8) is a viscid, colourless liquid, which has a pleasant pungent odour similar to that of menthol; when cooled in liquid air, it solidifies to a glassy mass filled with cracks, and becomes syrupy again at about − 30°. If small quantities are rapidly distilled under ordinary conditions, a little water seems to pass over at first, but then almost the whole quantity distils at 195—196° (743 mm.) apparently almost without decomposition.

The *phenylurethane*, $C_6H_{11}\cdot CMe_2\cdot O\cdot CO\cdot NH\cdot C_6H_5$, was prepared by mixing the alcohol (4·1 grams) with phenylcarbimide (3·5 grams); the mixture was left at the ordinary temperature for two days, heated at 60° for one hour, and then at 90° for another hour. The almost solid mass was spread on porous porcelain until dry, and purified by repeated recrystallisation from dilute methyl alcohol.

0·2500 gave 11·8 c.c. of nitrogen at 15° and 761 mm. N = 5·6.
$C_{16}H_{23}O_2N$ requires N = 5·4 per cent.

Normenthanolphenylurethane is readily soluble in methyl alcohol and crystallises from the diluted solvent in slender needles which melt at 86—87°.

$\Delta^{8(9)}$-*Normenthene*, $C_6H_{11}\cdot CMe\!:\!CH_2$.

Normenthanol(8) exhibits greater stability towards dehydrating agents than most of the analogously constituted tertiary alcohols, and in order to convert it into the hydrocarbon, prolonged boiling with potassium hydrogen sulphate was found to be necessary.

The crude alcohol, prepared from ethyl hexahydrobenzoate (30 grams) in the manner described in the last section, was digested with powdered potassium hydrogen sulphate (45 grams) for one and a half hours. Sufficient water was then added to dissolve the sulphate, and the oil extracted with ether and fractionated, when about half distilled below 170°. The remainder, which consisted mainly of unchanged alcohol, was again digested with potassium hydrogen sulphate, and the oil from both operations which distilled below 170° was several times fractionated, at first alone and then three times over sodium.

0·1985 gave 0·6320 CO_2 and 0·2283 H_2O. C = 86·8; H = 12·8.
C_9H_{16} requires C = 87·1; H = 12·9 per cent.

$\Delta^{8(9)}$-*Normenthene* boils at 157—158° and has a faint odour somewhat resembling that of parsley; it does not absorb oxygen from the

air, and is apparently not reduced when its solution in alcohol is treated with sodium.

It decolorises bromine readily with the formation of a dibromide, as the following experiment shows. The pure hydrocarbon (1·35 grams) was dissolved in twice its volume of chloroform, and, after cooling to $-10°$, a standard solution of bromine in chloroform was run in.

The colour disappeared instantly until 1·7 grams of bromine had been added, whereas, for the formation of a dibromide, 1·74 grams should have been absorbed. No evolution of hydrogen bromide was observed during this experiment, but after removing the chloroform by a current of dry air and leaving the residue in an exhausted desiccator over caustic potash and paraffin wax for two days, the oil had darkened in colour and some decomposition had taken place, as the following analysis shows:

0·2813 gave 0·3505 AgBr. Br = 53·0.
$C_9H_{16}Br_2$ requires Br = 56·3 per cent.

8-*Bromonormenthane*, $C_6H_{11}\cdot CBrMe_2$, *and Normenthane*, $C_6H_{11}\cdot CHMe_2$.

When normenthanol(8) is shaken in a stoppered bottle with five times its volume of fuming hydrobromic acid (saturated at 0°), it dissolves, and, in a few seconds, 8-bromonormenthane separates as an oil on the surface of the hydrobromic acid. After thoroughly shaking for half an hour, the stopper was tied down and the whole heated at 50° for fifteen minutes, water was then added, and the heavy oil extracted with carefully purified ether. The ethereal solution was washed three times with water, dried over calcium chloride, the bulk of the ether distilled off at as low a temperature as possible, and the oily residue left over sulphuric acid in an exhausted desiccator for 24 hours.

0·4632 gave 0·4204 AgBr. Br = 38·9.
$C_9H_{17}Br$ requires Br = 39·0 per cent.

When 8-*bromonormenthane* is distilled under 25 mm. pressure, almost the whole quantity passes over at 105° as a colourless oil, which possesses an unpleasant odour very similar to that of the higher bromides of the fatty series. An analysis of the distilled oil seems to indicate that during distillation slight decomposition takes place with elimination of traces of hydrogen bromide.

0·5904 gave 0·5298 AgBr. Br = 38·2.

8-Bromomenthane decomposes with formation of clouds of hydrogen bromide if an attempt is made to distil it under ordinary conditions.

In our experiments on the preparation of *normenthane*, 8-bromo-

normenthane was reduced, first with zinc dust and acetic acid and then with sodium and alcohol, and the hydrocarbon was freed from unsaturated impurity by oxidation with cold permanganate, the whole process being similar to that employed in the reduction of 8-bromo-*p*-menthane to *p*-menthane (p. 651). The hydrocarbon was then purified by three distillations over sodium.

0·1501 gave 0·4695 CO_2 and 0·1919 H_2O. C = 85·3 ; H = 14·2.
C_9H_{18} requires C = 85·7 ; H = 14·3 per cent.

Normenthane (*iso*propylhexamethylene) distils at 150—153° (755 mm.) and is a colourless, very volatile oil which possesses an odour closely resembling that of an aliphatic hydrocarbon. There does not appear to be any definite evidence that this interesting hydrocarbon had been previously obtained. Bamberger and Langfeld (*Ber.*, 1890, **23**, 1158) heated tetrahydroquinoline with hydriodic acid and phosphorus at 230° and obtained, in a yield of less than 0·25 per cent., a hydrocarbon which distilled at 146—148° (720 mm.), and which they considered might possibly be *iso*propylhexamethylene. A hydrocarbon, C_9H_{18}, has also been isolated from resin oil by Renard (*Ann. Chim. Phys.*, 1884, [vi], **1**, 229), which distils at 147—150° and may possibly be *iso*propylhexamethylene, but there does not seem to be sufficient evidence to justify its appearing under this name in Richter's *Lexikon* (vol. I, p. 643).

Phenyldimethylcarbinol, $C_6H_5·CMe_2·OH$.

This tertiary alcohol is readily obtained pure by the action of magnesium methyl iodide on ethyl benzoate. Ethyl benzoate (30 grams is added to an ethereal solution of magnesium methyl iodide (containing 9 grams of magnesium), and, after standing overnight, the product decomposed by dilute hydrochloric acid in the usual way.

The ethereal solution was evaporated and the residue digested with methyl-alcoholic potash (5 grams KOH) for 15 minutes ; water was then added and the oil again extracted with ether. Almost the whole quantity distilled at 114—115° (14 mm.), and when this was cooled in liquid air it solidified to a glassy mass filled with cracks.

As soon as the test-tube was removed from the liquid air, the glassy mass began to liquefy, but on rubbing the semi-solid substance with a glass rod it suddenly solidified to a hard mass of crystals.

The crystals were left in contact with porous porcelain until quite dry, and were then seen to consist of colourless needles.

0·2317 gave 0·6745 CO_2 and 0·1827 H_2O. C = 79·4 ; H = 8·8.
$C_9H_{12}O$ requires C = 79·4 ; H = 8·8 per cent.

Phenyldimethylcarbinol melts at about 35—37°, but owing to its

extreme solubility in the usual organic solvents no attempt was made to recrystallise it.

Phenyldimethylcarbinol had previously been prepared by Grignard (*Central Blatt.*, 1901, ii, **72**, 623) from acetophenone by the action of magnesium methyl iodide, and this chemist stated that it melts at 23° and distils at 91° (8 mm.). Klages (*Ber.*, 1902, **35**, 2636) shows that, when prepared in this way, the alcohol always contains some unchanged acetophenone, and this probably accounts for the fact that Grignard found a lower melting point than we did.

iso*Propenylbenzene*, $C_6H_5 \cdot CMe\colon CH_2$.

In preparing this hydrocarbon, crude phenyldimethylcarbinol was digested with potassium hydrogen sulphate for half an hour.

Water was added to dissolve the sulphate, and the oil, after extraction with ether, repeatedly fractionated, when almost the whole quantity distilled at 165° (764 mm.). This was twice distilled over sodium and analysed.

0·1795 gave 0·6031 CO_2 and 0·1357 H_2O. C = 91·6 ; H = 8·4.
C_9H_{10} requires C = 91·5 ; H = 8·5 per cent.

When cooled in liquid air, *iso*propenylbenzene crystallises in leaflets, and after removing from the liquid air a thermometer placed in the melting mass remained at −22° for a considerable time.

Klages (*loc. cit.*, p. 2640) had previously prepared *iso*propenylbenzene (methylvinylbenzene) from phenyldimethylcarbinol by the action of an excess of magnesium methyl iodide, and also Tiffeneau (*Compt. rend.*, 1902, **135**, 845) by distilling the same alcohol with anhydrous oxalic acid.

Action of Bromine.—*iso*Propenylbenzene (3·34 grams) was dissolved in twice its volume of chloroform, cooled to −10°, and titrated with a standard solution of bromine in chloroform, when 4·5 grams of bromine were decolorised, or almost exactly the quantity (4·53 grams) required for the formation of the dibromide. Attempts to purify the product by fractionation were unsuccessful, as although almost the whole quantity distilled at 147—150° (20 mm.), some hydrogen bromide was eliminated during the operation.

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LXVII.—*Some Derivatives of Anhydracetonebenzil.*

By Francis Robert Japp, F.R.S., and Joseph Knox, B.Sc., Carnegie Scholar in the University of Aberdeen.

The condensations of benzil with saturated aliphatic ketones to form anhydracetonebenzil and its homologues have been studied in considerable detail by one of us in conjunction with various collaborators. It appeared of interest to ascertain what course the reaction would take in the case of an unsaturated ketone and to compare the product with that obtained from the corresponding saturated ketone. We selected for this purpose, as an unsaturated ketone, methyl *iso*butenyl ketone, $CH_3{\cdot}CO{\cdot}CH{:}C(CH_3)_2$, and, as a saturated ketone, methyl *iso*butyl ketone.

Methyl *iso*butenyl ketone condenses with benzil under the influence of potassium hydroxide to form *β*-iso*propylideneanhydracetonebenzil*,

$$\begin{array}{l} C_6H_5{\cdot}C{=\!=}CH\diagdown \\ \quad\;\; | \qquad\qquad\;\; \rangle CO \\ C_6H_5{\cdot}C(OH){\cdot}C{=}C(CH_3)_2 \end{array}$$

(m. p. 205·5°), the reaction thus taking place exactly as in the case of the saturated ketones already studied, except that the presence of the bivalent *iso*propylidene group prevents the simultaneous formation of an isomeric *a*-compound. This condensation compound yields an *acetyl* derivative (m. p. 139—140° and 154—155°, dimorphous), the formation of which is rendered possible by the circumstance that the condensation compound has no hydrogen in the *β*-position, as otherwise derivatives of anhydracetonebenzil merely undergo dehydration under the influence of acetic anhydride. When reduced by brief boiling with hydriodic acid, *β*-*iso*propylideneanhydracetonebenzil yields *diphenyl*iso*propylidene*cyclo*pentenone*,

$$\begin{array}{l} C_6H_5{\cdot}C{\cdot}CH_2\diagdown \\ \quad\;\; \| \qquad\quad \rangle CO \\ C_6H_5{\cdot}C{-\!-}C{=}C(CH_3)_2 \end{array}$$

(m. p. 171°), the usual change in the position of the double bonds, so as to form a stilbene group, occurring during the process (compare Japp and Murray, Trans., 1897, 71, 145; Japp and Meldrum, 1901, 79, 1026).

Methyl *iso*butyl ketone and benzil, when condensed by means of potassium hydroxide, yield a mixture of *a*-iso*propylanhydracetonebenzil*,

$$\begin{array}{l} C_6H_5{\cdot}C{=\!=\!=\!=}C{-}CH(CH_3)_2 \\ \quad\;\; | \qquad\qquad\qquad \rangle CO \\ C_6H_5{\cdot}C(OH){\cdot}CH_2\diagup \end{array}$$

(m. p. 142°), and *β*-iso*propylanhydracetonebenzil*,

$$\begin{array}{l} C_6H_5{\cdot}C{=\!=}CH\diagdown \\ \quad\;\; | \qquad\qquad\quad \rangle CO \\ C_6H_5{\cdot}C(OH){\cdot}CH{-}CH(CH_3)_2 \end{array}$$

(m. p. 161·5°). The former compound condenses with benzaldehyde, under the influence

of potassium hydroxide, to yield *benzylidene-α-*iso*propylanhydracetone-benzil*,

$$\begin{array}{l} C_6H_5\cdot C{=\!=\!=}C{-}CH(CH_3)_2 \\ \quad\;| \qquad\qquad\quad >CO \\ C_6H_5\cdot C(OH)\cdot C{-}CH\cdot C_6H_5 \end{array}$$

(m. p. 179°).

We had originally contemplated carrying out the complete reduction of *β-iso*propylideneanhydracetonebenzil, and of one of the *iso*propylanhydracetonebenzils, with hydriodic acid and red phosphorus, so as to obtain, if possible, from both compounds the same hydrocarbon—diphenyl*iso*propyl*cyclo*pentane—and thus to prove more conclusively the relation existing between them; but the separation of the two *iso*propylanhydracetonebenzils was so difficult that we were compelled to relinquish our intention. Moreover, a preliminary experiment showed that the reduction of *β-iso*propylideneacetonebenzil beyond the *cyclo*pentenone stage did not yield a very satisfactory product.

At the end of the present paper we describe improved methods for the preparation of anhydracetonebenzil and β-methylanhydracetonebenzil.

Experimental.

I. *Condensation of Benzil with Methyl* iso*Butenyl Ketone.*

β-iso*Propylideneanhydracetonebenzil*,

$$\begin{array}{l} C_6H_5\cdot C{=}CH \\ \quad\;| \qquad\quad >CO \\ C_6H_5\cdot C(OH)\cdot C{=}C(CH_3)_2 \end{array}$$

.—Twenty grams of benzil, 15 grams of methyl *iso*butenyl ketone ("mesityl oxide"), and 15 c.c. of an aqueous solution of potassium hydroxide of 33·3 per cent. strength were introduced into a conical flask fitted with a condensing tube, and the whole was heated for 4 hours on a thin metal plate over a water-bath,* the flask being shaken from time to time. The product, which was very dark-coloured, was poured into warm water, when a black, oily substance separated; this was washed with water and then left until it became semi-solid, after which it was spread on a porous tile. The substance, freed from adhering oil, was recrystallised several times from hot benzene and was thus obtained in slender, yellow needles melting at 205·5°. The yield was 7 grams.

0·1632 gave 0·4929 CO_2 and 0·0911 H_2O. C = 82·37; H = 6·20.
$C_{20}H_{18}O_2$ requires C = 82·76; H = 6·20 per cent.

The same substance was obtained by condensing benzil with methyl *iso*butenyl ketone in the cold by means of a 0·5 per cent. solution of potassium hydroxide in absolute alcohol; but the yield was even poorer than in the preceding case.

* This arrangement gives a temperature of from 60° to 70°, provided that no steam is allowed to condense between the plate and the flask.

A portion of the substance was heated for 10 minutes at 310° (diphenylamine vapour) in an atmosphere of carbon dioxide. It resolidified on cooling and, after recrystallisation from benzene, was found to consist of unchanged substance (m. p. 205·5°). A sublimate which had formed in the upper part of the tube gave the same melting point.

The foregoing result shows that the condensation product is a closed-chain compound, inasmuch as all open-chain compounds formed by the condensation of benzil with ketones are changed on heating, yielding closed-chain compounds. Thus desylene-methyl ethyl ketone is in this way transformed into β-methylanhydracetonebenzil (Japp and Meldrum, Trans., 1901, **79**, 1031).

An attempt to synthesise β-*iso*propylideneanhydracetonebenzil by condensing acetone with anhydracetonebenzil under the influence of alcoholic potassium hydroxide—a process which, if benzaldehyde be substituted for acetone, readily yields benzylideneanhydracetonebenzil—led to no result.

Acetyl Derivative.—One gram of β-*iso*propylideneanhydracetonebenzil and 10 grams of acetic anhydride were mixed, and 1 drop of concentrated sulphuric acid was added. (If this proportion of acid is exceeded, a very impure product is obtained.) This addition caused the solid substance to dissolve, yielding a dark brown solution. After three days the mixture was poured into excess of water, and the yellow, flocculent precipitate which gradually separated, was purified by recrystallisation, first from alcohol, afterwards from benzene with addition of light petroleum (sp. gr. 0·71—0·72), and finally from light petroleum alone. It was thus obtained in slender, colourless needles. It melts at 139—140° and, if kept a little above this temperature, resolidifies, finally melting at 154—155°. This phenomenon is doubtless due to dimorphism, and not to chemical change, inasmuch as a specimen which had been melted as above, then allowed to cool, and recrystallised from light petroleum, again gave the same two melting points.

Analysis showed that a *monacetyl* derivative had been formed.

0·1566 gave 0·4570 CO_2 and 0·0857 H_2O. C = 79·58 ; H = 6·08.

$C_{22}H_{20}O_3$ requires C = 79·51 ; H = 6·02 per cent.

β-*iso*Propylideneanhydracetonebenzil is not acetylated by boiling it for 4 hours with a mixture of acetic anhydride and anhydrous sodium acetate.

*Reduction of β-*iso*Propylideneanhydracetonebenzil with Hydriodic Acid: Formation of Diphenyl*iso*propylidene*cyclo*pentenone,*

$$\begin{array}{l} C_6H_5\cdot C\cdot CH_2\diagdown \\ \quad\quad \| \quad\quad\quad\quad >CO \\ C_6H_5\cdot C\text{——}C\text{=}C(CH_3)_2 \end{array} .$$

—Two grams of *β-iso*propylideneanhydracetonebenzil (m. p. 205·5°) were boiled for 8 minutes with 40 grams of fuming hydriodic acid (sp. gr. 1·96). Water was added, the organic substance was dissolved in ether, and the ethereal solution was shaken successively with aqueous sulphurous acid, sodium carbonate solution, and water. During the latter part of the process, a crystalline substance separated from the ether; it was filtered off and recrystallised from benzene, from which it was deposited in thick prisms melting constantly at 171°. The dried ethereal filtrate, on evaporation, yielded a further quantity of this substance, which was purified in the same way. Yield: 0·6 gram.

0·1448 gave 0·4647 CO_2 and 0·0863 H_2O. C = 87·52; H = 6·62.
$C_{20}H_{18}O$ requires C = 87·59; H = 6·57 per cent.

II. *Condensation of Benzil with Methyl* iso*Butyl Ketone.*

α-iso*Propylanhydracetonebenzil*,

$$\begin{array}{l} C_6H_5\cdot C\!=\!\!=\!\!=\!\!=\!C\!-\!CH(CH_3)_2, \\ \quad | \qquad\qquad\quad >CO \\ C_6H_5\cdot C(OH)\cdot CH_2 \end{array}$$

and

β iso*Propylanhydracetonebenzil*,

$$\begin{array}{l} C_6H_5\cdot C\!=\!\!=\!\!=\!CH \\ \quad | \qquad\qquad\quad >CO \\ C_6H_5\cdot C(OH)\cdot CH\!-\!CH(CH_3)_2 \end{array}.$$

—Forty grams of finely powdered benzil, 28 grams of methyl *iso*butyl ketone, and 400 c.c. of a 0·5 per cent. solution of potassium hydroxide in absolute alcohol were shaken in a corked flask until the benzil had dissolved, after which the mixture was left for 12 days. The solution was then diluted with water until it became turbid, and allowed to crystallise. The crystalline deposit, which weighed 51 grams, proved to be a mixture of two substances—one of them dimorphous—which were very difficult to separate. Fractional crystallisation proved unavailing, although nearly all the ordinary organic solvents were tried. Finally we had to resort to the tedious process of picking out the different kinds of crystals. The crystalline product was dissolved in benzene, and somewhat less than an equal volume of light petroleum (sp. gr. 0·71—0·72) was added. The solution deposited colourless, six-sided prisms, white, silky needles, and flat, yellow prisms. The three kinds of crystals were separated mechanically.

The six-sided prisms were recrystallised repeatedly from benzene with the addition of light petroleum until they showed the constant melting point of 142°. The white, silky needles also melted at 142°, and a mixture of these with the six-sided prisms gave no depression of melting point. When either the six-sided prisms or the silky needles are crystallised from benzene with addition of light petroleum, a mixture of prisms and needles is obtained in each case. When a

mixture of the prisms and needles is allowed to stand with a mixture of benzene and light petroleum insufficient to dissolve them, the needles gradually disappear, being transformed into the prisms. The substance melting at 142° is thus dimorphous, the six-sided prisms being the stable form at the ordinary temperature. This substance is α-iso*propylanhydracetonebenzil*, as is shown by its yielding a benzylidene derivative (*v. infra*).

0·2151 gave 0·6477 CO_2 and 0·1339 H_2O. C = 82·12 ; H = 6·91.
$C_{20}H_{20}O_2$ requires C = 82·19 ; H = 6·84 per cent.

This compound (m. p. 142°) was recovered unchanged after being heated for 5 minutes at 330° in an atmosphere of carbon dioxide. This result indicates that the substance is a closed-chain condensation product, as formulated.

The flat, yellow prisms were recrystallised from light petroleum (sp. gr. 0·71—0·72). The compound, which is β-iso*propylanhydracetonebenzil*, was thus obtained in flat, colourless needles, melting constantly at 161·5°. β-Monalkylanhydracetonebenzils melt higher than the corresponding α-derivatives.

0·1563 gave 0·4711 CO_2 and 0·0980 H_2O. C = 82·20 ; H = 6·96.
$C_{20}H_{20}O_2$ requires C = 82·19 ; H = 6·84 per cent.

The quantity of this compound was too small, and its separation too difficult, to allow of our investigating it further.

Benzylidene-α-iso*propylanhydracetonebenzil*,

$$\begin{array}{l} C_6H_5\cdot C \!=\!=\!=\! C\!\diagdown\!CH(CH_3)_2 \\ \qquad\quad | \qquad\qquad >CO \\ C_6H_5\cdot C(OH)\cdot C\!=\!CH\cdot C_6H_5 \end{array} .$$

—One gram of α-*iso*propylanhydracetonebenzil (m. p. 142°) and 0·4 gram of benzaldehyde were shaken with a 1 per cent. solution of potassium hydroxide in absolute alcohol until the whole dissolved. After 12 days the liquid was diluted with half its volume of water. The crystals which were deposited weighed 1 gram. They were twice recrystallised from benzene, with the addition of light petroleum, and were thus obtained in the form of four-sided prisms, with oblique or pointed ends. They melted constantly at 179°.

0·1623 gave 0·5062 CO_2 and 0·0948 H_2O. C = 85·06 ; H = 6·49.
$C_{27}H_{24}O_2$ requires C = 85·26 ; H = 6·31 per cent.

III. *Improved Methods of Preparing Anhydracetonebenzil and β-Methylanhydracetonebenzil.*

Anhydracetonebenzil.—Acetonebenzil, $\begin{array}{l} C_6H_5\cdot CO \\ C_6H_5\cdot C(OH)\cdot CH_2\cdot CO\cdot CH_3 \end{array}$, and

anhydracetonebenzil, $\begin{matrix} C_6H_5\cdot C = CH \\ C_6H_5\cdot C(OH)\cdot CH_2 \end{matrix} > CO$, were first prepared by Japp and Miller (Trans., 1885, **47**, 21 and 27), who, however, assigned to the latter compound a constitution different from the foregoing and termed it "dehydracetonebenzil." The former compound was obtained by the action of a small quantity of aqueous potassium hydroxide on a mixture of benzil and acetone, the latter was formed from the same substances when an excess of potassium hydroxide was used.

Both of these substances were subsequently prepared on several occasions; but the yields varied in an unaccountable manner. It was evident that much depended on the character of the acetone. Japp and Miller found that a specimen of acetone purified merely by fractional distillation could not be used in the preparation of acetonebenzil. They say: "The employment of an acetone purified by means of the bisulphite compound is in this reaction *indispensable*—not merely for obtaining a good yield of the compound, but in order to obtain any of the compound at all." Japp and Klingemann, however (Trans., 1890, **57**, 673, footnote), found that acetone could be prepared so pure as not to give the reaction, but that the same acetone readily condensed with benzil under the influence of a little aqueous potassium hydroxide to form acetonebenzil, if two or three drops of alcohol were previously added to it.*

We have now had a similar experience in the preparation of anhydracetonebenzil. Working according to the directions given by Japp and Lander (Trans., 1897, **71**, 130), who improved upon the original process, and using Kahlbaum's "acetone from the bisulphite compound," we obtained hardly any anhydracetonebenzil, the greater part of the benzil being recovered unchanged. This was the more surprising, as Japp and Lander, in preparing the very large quantities of anhydracetonebenzil which they required for their study of the oxidation of this compound, had not merely employed this method, but had used acetone of the same quality, also obtained from Kahlbaum, although of a different preparation.

Mindful of Japp and Klingemann's experience with acetonebenzil, we repeated the process, adding, however, a few drops of alcohol to the mixture. The effect was such that we obtained a yield even better than that recorded by Japp and Lander.

As this slight modification may thus mean all the difference between failure and success in the preparation of anhydracetonebenzil, and as it renders the course of the reaction independent of minute differences

* I pointed out (*loc. cit.*) that the "pure" acetone prepared by Dr. Miller and myself may have contained traces of alcohol derived from the commercial ether which was used in washing the bisulphite compound.—F. R. J.

in the quality of the acetone employed, we will describe the method in detail.

Two hundred grams of finely-powdered benzil, 125 grams of pure acetone (Kahlbaum's acetone "from the bisulphite compound"), 1 c.c. of alcohol, and 2 c.c. of an aqueous solution of potassium hydroxide of 33·3 per cent. strength were shaken in a corked flask until the whole of the benzil had dissolved. The liquid became slightly warm during the process, owing to the formation of the aldol condensation compound, acetonebenzil. Fifty more c.c. of the aqueous potassium hydroxide were then added, and the mixture was warmed for half an hour on the water-bath, during which time it was frequently shaken. The whole was then poured into hot water, and the organic substance, which solidified on cooling, was ground in a mortar, washed, first with hot water and then with a little ether to remove dark-coloured impurities, and finally recrystallised from hot benzene. In this way we obtained, from the foregoing quantities, 165 grams of anhydracetonebenzil (m. p. 147° *), without working up the mother liquors, whereas Japp and Lander, who did not add alcohol to the mixture, obtained only 150 grams in all.

It must be borne in mind that although the addition of a small quantity of alcohol thus facilitates the occurrence of the reaction, the condensation of benzil and acetone to form anhydracetonebenzil cannot be effected by means of an alcoholic solution of potassium hydroxide, since under these circumstances the anhydracetonebenzil formed in the first instance condenses with a second molecule of benzil to form anhydracetonedibenzil.

β-Methylanhydracetonebenzil.—Of the two monomethyl homologues of anhydracetonebenzil—α-methylanhydracetonebenzil,

$$\begin{matrix} C_6H_5{\cdot}C{=}C(CH_3) \\ C_6H_5{\cdot}C(OH){\cdot}CH_2 \end{matrix}\!\!>CO,$$

and β-methylanhydracetonebenzil, $\begin{matrix} C_6H_5{\cdot}C{=\!=\!=}CH \\ C_6H_5{\cdot}C(OH){\cdot}CH(CH_3) \end{matrix}\!\!>CO$ — the α-compound is readily obtained, together with only a mere trace of the β-compound, by the protracted action of a 0·5 per cent. solution of potassium hydroxide in absolute alcohol on a mixture of benzil and methyl ethyl ketone in the cold; whereas, when *aqueous* potassium hydroxide of 33·3 per cent. strength is used, and the mixture is heated,

* This is the melting point of *yellow* anhydracetonebenzil as ordinarily obtained, the yellow colour being due to the presence of a trace of benzylideneanhydracetonebenzil which cannot be removed except by a wasteful process of partial oxidation of the substance. The pure compound is colourless and melts at 149°, but the yellow substance is sufficiently pure for all ordinary purposes (compare Japp and Miller, Trans., 1885, **47**, 27; Japp and Findlay, 1899, **75**, 1018 and 1019).

the proportion of β-compound formed is increased, remaining, however, below that of the α-compound which is simultaneously produced, so that the yield of β-compound still leaves much to be desired (Japp and Meldrum, Trans., 1901, **79**, 1028).

We now find that by substituting aqueous sodium hydroxide for potassium hydroxide in the latter reaction the yield of β-compound is very appreciably improved.

Eighty grams of benzil, 50 grams of methyl ethyl ketone, 0·5 c.c. of alcohol, and 60 c.c. of a solution of sodium hydroxide prepared by dissolving the *commercial* * hydroxide in twice its weight of water, were introduced into a conical flask fitted with a condensing tube, and the whole was heated for 3½ hours on a thin metal plate over a water-bath, the flask being shaken from time to time. The product was poured into hot water, and the solidified substance was ground, washed with water, freed from dark-coloured impurities by treatment with a little ether, and dissolved in boiling alcohol. The solution, on cooling, deposited 24 grams of practically pure β-methylanhydracetonebenzil. The mother liquor contained α-methylanhydracetonebenzil and α-desylenemethyl ethyl ketone, together with a small quantity of β-methylanhydracetonebenzil; these could be separated by fractional crystallisation from alcohol. It is to be noted that desylenemethyl ethyl ketone can be converted quantitatively into β-methylanhydracetonebenzil by heating it for a short time at 330° (Japp and Meldrum, Trans., 1901, **79**, 1031).

A second experiment conducted in the same way also gave 24 grams of the β-compound, whereas in a previous experiment in which the same quantities of benzil and methyl ethyl ketone were heated with aqueous *potassium* hydroxide of 33·3 per cent. strength only 19 grams were obtained.

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* In one experiment, in which we employed *pure* sodium hydroxide, the solution made up in the above proportions proved to be too strong, and considerable resinification of the organic substances occurred.

LXVIII.—*The Dihydrocyanides of Benzil and Phenanthraquinone. Second Notice.**

By Francis Robert Japp, F.R.S., and Joseph Knox, B.Sc., Carnegie Scholar in the University of Aberdeen.

Although the dihydrocyanides of α-diketones are most generally formulated as tartronitriles, no strict proof that they possess this constitution has hitherto been given, with the exception of the hydrolysis of Zinin's benzildihydrocyanide, $\begin{array}{l}C_6H_5\cdot C(OH)\cdot CN \\ C_6H_5\cdot C(OH)\cdot CN\end{array}$, to diphenyltartramide (Burton, *Ber.*, 1883, **16**, 2232). Indeed, owing to the ease with which these compounds break up into α-diketone and hydrocyanic acid, some writers have preferred to represent them as molecular combinations.

We have obtained conclusive evidence of the tartronitrile constitution of these compounds by preparing their *diacetyl* derivatives. The dihydrocyanides which we have studied in this direction are: (1) benzildihydrocyanide; (2) the phenanthraquinonedihydrocyanide obtained by Japp and Miller; and (3) a stereoisomeric phenanthraquinonedihydrocyanide described in the present paper.

By treatment with concentrated sulphuric acid in the cold, benzildihydrocyanide is converted into *diphenylacetamide.* In order to account for this reaction it is necessary to assume that, as a first stage, a pinacoline migration occurs:

$$\begin{array}{l}C_6H_5\cdot C(OH)\cdot CN \\ C_6H_5\cdot C(OH)\cdot CN\end{array} \longrightarrow \begin{array}{l}(C_6H_5)_2C\cdot CN \\ \quad\quad\;\; C(OH)_2\cdot CN\end{array},$$

the resulting compound then undergoing hydrolytic fission with formation of diphenylacetamide, $(C_6H_5)_2CH\cdot CONH_2$, and possibly oxalic acid.

By the interaction of phenanthraquinone with 30 per cent. aqueous hydrocyanic acid in the cold, Japp and Miller (Trans., 1887, **51**, 32) obtained a phenanthraquinonedihydrocyanide crystallising in slender needles. We find that a stronger solution of hydrocyanic acid is practically without action on phenanthraquinone in the cold, but that, on heating the mixture at 50°, a *stereoisomeric phenanthraquinonedihydrocyanide*, crystallising in laminæ, is formed. The laminar crystals have a higher decomposing point than the acicular. On the other hand, the diacetyl derivative of the laminar compound melts lower than that of the acicular compound. The best yield of the laminar compound is obtained by employing anhydrous hydrocyanic acid.

* See Japp and Miller, Trans., 1887, **51**, 29.

The reactions of the two phenanthraquinonedihydrocyanides show that both have the structural formula $\begin{matrix} C_6H_4\cdot C(OH)\cdot CN \\ | \quad\quad | \\ C_6H_4\cdot C(OH)\cdot CN \end{matrix}$. They must therefore be stereoisomerides, the one being the racemic, the other the meso-form, although it is at present impossible to assign to each its specific configuration.

By hydrolysing acicular phenanthraquinonedihydrocyanide, not previously freed from adhering hydrocyanic acid, with fuming hydrochloric acid in the cold, Japp and Miller (*loc. cit.*) obtained two compounds, $C_{15}H_9ON$ (m. p. 241°) and $C_{15}H_{11}O_2N$ (m. p. 183°), both of which yield salts with bases, the former compound taking up water in the process, so that its dehydrated sodium salt, for example, has the formula $C_{15}H_{10}O_2NNa$; but it again parts with water when liberated from its salts, yielding the original compound, $C_{15}H_9ON$ (compare Japp and Miller). From a study of the reactions of these compounds we assign to them the constitutional formulæ

$$\begin{matrix} C_6H_4\cdot C\cdot CO \\ | \quad\; \| \quad | \\ C_6H_4\cdot C\cdot NH \end{matrix} \quad \text{and} \quad \begin{matrix} C_6H_4\cdot C(OH)\cdot CO \\ | \quad\quad | \quad\quad | \\ C_6H_4\cdot CH\text{---}NH \end{matrix}$$

Phenanthranil (m. p. 241°). Hydroxydihydrophenanthranil (m. p. 183°).

Both compounds are capable of interacting also in the tautomeric form, and we are unable to say whether the free substances are lactams, as here represented, or the corresponding lactims. The metallic salts formed from phenanthranil are salts of the unstable phenanthranilic acid, $\begin{matrix} C_6H_4\cdot C\cdot CO_2H \\ | \quad\; \| \\ C_6H_4\cdot C\cdot NH_2 \end{matrix}$, which, as just mentioned, when liberated from its salts, parts with water, regenerating phenanthranil. Phenanthranil yields a *monacetyl* derivative, $\begin{matrix} C_6H_4\cdot C\cdot CO \\ | \quad\; \| \quad | \\ C_6H_4\cdot C\cdot N\cdot C_2H_3O \end{matrix}$. Two esters correspond with it: one is *ethyl phenanthranilate*,

$$\begin{matrix} C_6H_4\cdot C\cdot CO_2C_2H_5 \\ | \quad\; \| \\ C_6H_4\cdot C\cdot NH_2 \end{matrix},$$

and the other is the *lactim ester** of phenanthranil, $\begin{matrix} C_6H_4\cdot C\cdot C\cdot OC_2H_5 \\ | \quad\; \| \quad \| \\ C_6H_4\cdot C\cdot N \end{matrix}$. Both esters, when hydrolysed with sodium hydroxide, yield *sodium phenanthranilate* ; but a portion of the lactim ester is transformed, at the same time, into the non-hydrolysable *hydroxyethyldihydrophen-*

* We would suggest that compounds of this type should be called *esters* rather than *ethers*. Thus, in the complex –C(NH)·OAlk of the so-called *imido-ethers*, the imido-group has, structurally, the same function as the doubly-linked oxygen in the complex –CO·OAlk of the ordinary esters, and the name *imido-ester* would indicate more clearly this analogy.

anthranil, $\begin{array}{l} C_6H_4\cdot C(OH)\cdot CO \\ | \qquad\quad | \qquad\qquad | \\ C_6H_4\cdot CH\text{——}N\cdot C_2H_5 \end{array}$, the ethyl group migrating in the process.

Hydroxydihydrophenanthranil, $\begin{array}{l} C_6H_4\cdot C(OH)\cdot CO \\ | \qquad\quad | \qquad\qquad | \\ C_6H_4\cdot CH\text{——}NH \end{array}$, dissolves in sodium carbonate, yielding a sodium salt which is probably

$$\begin{array}{l} C_6H_4\cdot C(OH)\cdot C\cdot ONa \\ | \qquad\quad | \qquad\quad \| \\ C_6H_4\cdot CH\text{——}N \end{array},$$

but was not obtained in a condition suitable for analysis (compare Japp and Miller, *loc. cit.*, p. 35) and which, when its aqueous solution is digested for some time on the water-bath, decomposes, depositing a brown amorphous substance. Acetylated in the cold with acetic anhydride to which a little concentrated sulphuric acid has been added, hydroxydihydrophenanthranil yields a *monacetyl* derivative,

$$\begin{array}{l} C_6H_4\cdot C(OH)\cdot CO \\ | \qquad\quad | \qquad\qquad | \\ C_6H_4\cdot CH\text{——}N\cdot C_2H_3O \end{array},$$

insoluble in sodium carbonate. Treated with sodium ethoxide and ethyl iodide, hydroxydihydrophenanthranil yields the above-mentioned *hydroxyethyldihydrophenanthranil,* $\begin{array}{l} C_6H_4\cdot C(OH)\cdot CO \\ | \qquad\quad | \qquad\qquad | \\ C_6H_4\cdot CH\text{——}N\cdot C_2H_5 \end{array}$, in which the ethyl is doubtless attached to nitrogen, as the compound is not hydrolysed by warming it with alcoholic potassium hydroxide and is moreover insoluble in aqueous caustic alkalis, showing that the labile hydrogen atom has been replaced by ethyl; this ethyl derivative yields a *monacetyl* derivative, $\begin{array}{l} C_6H_4\cdot C(O\cdot C_2H_3O)\cdot CO \\ | \qquad\quad | \qquad\qquad\qquad\quad | \\ C_6H_4\cdot CH\text{————}N\cdot C_2H_5 \end{array}$. Warmed with benzaldehyde, hydroxydihydrophenanthranil is converted into a *benzylidene* derivative, probably derived from the lactim form and having the constitution,

$$\begin{array}{l} \qquad\quad CH\cdot C_6H_5 \\ \qquad\quad / \quad \backslash \\ \qquad\;\; O \qquad O \\ \qquad\;\; | \qquad\; | \\ C_6H_4\cdot C\text{—}C \\ | \qquad\quad | \quad\; \| \\ C_6H_4\cdot CH\cdot N \end{array};$$

it would thus be an analogue of chloralide; it is insoluble in caustic alkalis. The foregoing ethyl derivative of hydroxydihydrophenanthranil, as might be expected from its constitution, does not interact with benzaldehyde.

On the other hand, we must point out that sodium phenanthranilate and ethyl phenanthranilate, although, as above formulated, they contain an amino-group, do not interact with benzaldehyde.

At first we were inclined to regard the compound (m. p. 183°), which we have formulated as hydroxydihydrophenanthranil, as phenanthranilic (10-aminophenanthrene-9-carboxylic) acid. This view is, however, untenable, as it would involve the identity of the totally

distinct sodium salts and ethyl esters of the unstable phenanthranilic acid from phenanthranil with those of hydroxydihydrophenanthranil. Besides, there would be no reason why the closed side chain of phenanthranil, when once opened, should spontaneously close again. Nor would such a formula for hydroxydihydrophenanthranil explain the insolubility of the benzylidene and acetyl derivatives of this compound in alkalis, as also the fact that its ethyl derivative is not only insoluble in, but not hydrolysable by, alkalis. It would be necessary, at all events, to assume that phenanthranil and hydroxydihydrophenanthranil contain different hydrocarbon nuclei: that in one of them, possibly the well-known change to the diphenylenemethane nucleus, as in the formation of diphenyleneglycollic acid from phenanthraquinone, has taken place; and, that this is not the case, is shown by the following experiments:

If hydroxydihydrophenanthranil is heated in a sealed tube with fuming hydrochloric acid it yields 9-*hydroxyphenanthrene*,

$$\begin{array}{l} C_6H_4\cdot CH \\ | \qquad \ \ \| \\ C_6H_4\cdot C\cdot OH \end{array},$$

together with the corresponding 9-*phenanthryl oxide*,

$$\begin{array}{l} C_6H_4\cdot CH \qquad HC\cdot C_6H_4 \\ | \qquad \ \ \| \qquad\quad \| \quad\ | \\ C_6H_4\cdot C{-}O{-}C\cdot C_6H_4 \end{array},$$

and *tetraphenylenefurfuran*, $\begin{array}{l} C_6H_4\cdot C{-}{-}C\cdot C_6H_4 \\ | \qquad \ \ \| \quad \ \| \quad | \\ C_6H_4\cdot C \quad C\cdot C_6H_4 \\ \qquad\quad \diagdown \diagup \\ \qquad\quad\ \ O \end{array}$, the two last-mentioned compounds being formed from the first (compare Japp and Findlay, Trans., 1897, **71**, 1115). If phenanthranil is treated in the same way, it undergoes the same changes, except that a higher temperature is required owing to the greater stability of the compound. As we were compelled to employ a smaller quantity of phenanthranil for the reaction, we contented ourselves with isolating the primary product—which is also the chief product—9-*hydroxyphenanthrene*.

Both phenanthranil and hydroxydihydrophenanthranil therefore contain the phenanthrene nucleus.

The mechanism of the decomposition may, in the case of phenanthranil, be formulated as follows:

$$\begin{array}{l} C_6H_4\cdot C\cdot CO \\ | \qquad \ \ \| \quad | \\ C_6H_4\cdot C\cdot NH \end{array} \xrightarrow{H_2O} \begin{array}{l} C_6H_4\cdot C\cdot CO_2H \\ | \qquad \ \ \| \\ C_6H_4\cdot C\cdot NH_2 \end{array} \longrightarrow \begin{array}{l} C_6H_4\cdot CH \\ | \qquad \ \ \| \\ C_6H_4\cdot C\cdot NH_2 \end{array};$$

then

$$\begin{array}{l} C_6H_4\cdot CH \\ | \qquad \ \ \| \\ C_6H_4\cdot C\cdot NH_2 \end{array} + H_2O + HCl = \begin{array}{l} C_6H_4\cdot CH \\ | \qquad \ \ \| \\ C_6H_4\cdot C\cdot OH \end{array} + NH_4Cl$$

(Japp and Findlay, *loc. cit.*, p. 1117).

We studied the conditions of the hydrolysis of acicular phenanthra-

quinonedihydrocyanide much more thoroughly than had been done by Japp and Miller. A product of the hydrolysis which had been overlooked by them is *diphenylenetartramide*, $\begin{matrix} C_6H_4\cdot C(OH)\cdot CONH_2 \\ | \qquad\quad | \\ C_6H_4\cdot C(OH)\cdot CONH_2 \end{matrix}$.

Our attempts to hydrolyse the laminar phenanthraquinone dihydrocyanide were only partially successful, as the reaction does not occur except at a temperature at which the greater part of the substance is resinified. *Phenanthranil* and *hydroxydihydrophenanthranil* were isolated from the product.

Experimental.

Benzildihydrocyanide.

Acetylation of Benzildihydrocyanide.—The benzildihydrocyanide used in this and the following experiments was prepared by Zinin's method as modified by Japp and Miller (Trans., 1887, **51**, 31).

In acetylating the compound, a mixture of 15 grams of acetic anhydride and 4 drops of concentrated sulphuric acid was added to 7 grams of finely-powdered benzildihydrocyanide, and the whole was allowed to stand in the cold for three weeks. The solid was separated by filtration and recrystallised from boiling glacial acetic acid. The yield of recrystallised substance was 6 grams. It crystallised in six-sided plates, or long pointed needles, both of which showed straight extinction, and melted, when rapidly heated, with decomposition at 242°.

Analysis gave figures agreeing with the formula of *diacetylbenzildihydrocyanide*, $\begin{matrix} C_6H_5\cdot C(O\cdot C_2H_3O)\cdot CN \\ | \\ C_6H_5\cdot C(O\cdot C_2H_3O)\cdot CN \end{matrix}$.

0·2079 gave 0·5242 CO_2 and 0·0881 H_2O. C = 68·76 ; H = 4·70.
0·2834 ,, 20·05 c.c. moist nitrogen at 8° and 741 mm. N = 8·32.
$C_{20}H_{16}O_4N_2$ requires C = 68·96 ; H = 4·59 ; N = 8·04 per cent.

Action of Concentrated Sulphuric Acid on Benzildihydrocyanide: Formation of Diphenylacetamide, $(C_6H_5)_2CH\cdot CONH_2$.—Forty grams of finely-powdered benzildihydrocyanide were sifted into 400 grams of concentrated sulphuric acid, whilst the mixture was constantly stirred. The whole was allowed to stand for 40 hours, after which it was poured on to pounded ice. The solid substance was separated by filtration and the acid solution was evaporated on the water-bath.

The solid substance was digested with sodium carbonate, which extracted a yellow acid, but in quantity too small for further investigation. The solid residue remaining after this treatment was thoroughly washed with ether, to remove resinous matters. (If the washing with ether has not been sufficient, the residue cannot be induced to crystallise.) The washed residue was recrystallised first

from alcohol, and afterwards from benzene. It was somewhat difficult to purify, but was ultimately obtained in pointed, or obliquely truncated, flat prisms, with an extinction angle of 44—45° from the long axis, and melting at 167·5—168°.

The above-mentioned acid solution yielded, on evaporation, an oil, which solidified on standing. It was boiled with sodium carbonate, and the residue, recrystallised from the foregoing solvents, yielded a further quantity of the substance melting at 167·5—168°. The substance thus obtained was free from resin and was much easier to purify than the original solid residue.

0·2081 gave 0·6048 CO_2 and 0·1181 H_2O. C = 79·26; H = 6·30.
0·2079 „ 0·6041 CO_2 „ 0·1195 H_2O. C = 79·24; H = 6·38.
0·1002 „ 5·95 c.c. moist nitrogen at 20·5° and 759 mm. N = 6·76.
$C_{14}H_{13}ON$ requires C = 79·62; H = 6·16; N = 6·63 per cent.

The compound is *diphenylacetamide*, $(C_6H_5)_2CH\cdot CONH_2$. It was further identified by comparison with a specimen of this substance prepared by heating ammonium diphenylacetate in a sealed tube at 230° (Neure, *Annalen*, 1888, **250**, 141). The melting points, mixture melting point, crystalline form and optical properties of the two preparations were identical. Both Neure, and Anschütz and Römig (*Annalen*, 1886, **233**) give the melting point of diphenylacetamide at 165—166°; but we confirmed the somewhat higher melting point of 167·5—168°, above given, by a determination with a normal thermometer.

The action of hydrochloric acid on benzildihydrocyanide was also studied, but did not yield results of interest. By heating the substance in a sealed tube with fuming aqueous hydrochloric acid the only products obtained were benzoic acid and an uncrystallisable oil. By allowing benzildihydrocyanide to stand with alcoholic hydrogen chloride in the cold, only a hydrochloride of the dihydrocyanide was formed.

*Isomeric Phenanthraquinonedihydrocyanides.**

Acicular Phenanthraquinonedihydrocyanide.—In preparing this compound one of the methods devised by Japp and Miller (*loc. cit.*, p. 33) was employed. Finely powdered phenanthraquinone was allowed to stand for 4—5 days in a strong corked flask with a considerable excess of 30 per cent. aqueous hydrocyanic acid, and the mixture was shaken from time to time. At the end of this time the orange-coloured

* In preparing these compounds, it is essential to employ a phenanthraquinone that has been purified by means of its hydrogen sodium sulphite compound, as otherwise the anthraquinone which is invariably present in specimens of phenanthraquinone which have been purified merely by recrystallisation will contaminate the products.

particles of the phenanthraquinone had disappeared and the flask contained a magma of white, needle-shaped crystals. The substance was freed from the adhering liquid by means of a filter-pump, and then dried in a vacuum desiccator over sulphuric acid. It turns reddish-brown on drying, owing to a partial regeneration of phenanthraquinone.

Japp and Miller purified the substance for analysis by washing it with chloroform, which readily dissolves the phenanthraquinone but in which the dihydrocyanide is practically insoluble. We found, however, that the dihydrocyanide can be recrystallised from hot benzene, provided that too long boiling is avoided. It was deposited in colourless needles, which, when heated in a capillary tube, decompose and turn red at a temperature below 100°.

0·1662 gave 15·1 c.c. moist nitrogen at 13° and 746 mm. N = 10·53.
$C_{16}H_{10}O_2N_2$ requires N = 10·69 per cent.

Sometimes the hot benzene solution deposited at first colourless six-sided plates and afterwards needles. We were at first inclined to think that these plates were the stereoisomeric laminar phenanthraquinonedihydrocyanide (to be described later on). On separating some of these plates, however, we found that they showed the same decomposing point as the needles, whereas the laminar form does not decompose until 160—170°, and that their diacetyl derivative melted at 255—256°, the melting point of the diacetyl derivative of the needles, and showed no depression when mixed with a specimen of the latter substance. The difference was, therefore, doubtless nothing more than a difference in crystalline habit.

The following experiments on the loss of weight which acicular phenanthraquinonedihydrocyanide, purified by recrystallisation from benzene, suffers on heating, are of interest. The substance was heated at the respective temperatures until the weight remained constant.

0·6374 lost, on heating at 100° for 2 hours, 0·1314 = 20·61 per cent.
$C_{16}H_{10}O_2N_2$ – 2HCN requires a loss = 20·61 per cent.

The substance which remained was phenanthraquinone.

0·2102 lost, on heating at 70° for 11 hours (weight constant), 0·0217 = 10·32 per cent.
$C_{16}H_{10}O_2N_2$ – HCN requires a loss = 10·30 per cent.

The substance which remained in the latter case was a scarlet powder and was doubtless *phenanthraquinonemonohydrocyanide*. Its solution in hot benzene deposited scarlet crystals, but a portion of it was decomposed in the process into phenanthraquinone and hydrocyanic acid.

The experiment just described shows that phenanthraquinonedihydrocyanide, when heated for a long time, shows a much lower decomposing point than that (a little under 100°) indicated by its behaviour when quickly heated in a melting-point tube.

Acetylation of Acicular Phenanthraquinonedihydrocyanide.—Twenty grams of acetic anhydride containing 5 drops of concentrated sulphuric acid were added to 10 grams of powdered acicular phenanthraquinonedihydrocyanide. There was a slight rise of temperature on mixing, and the flask was therefore cooled with water. The dihydrocyanide dissolved completely, and in less than an hour crystals began to form. After two days the contents of the flask had almost solidified to a mass of colourless crystals. After recrystallisation from boiling glacial acetic acid, the substance was obtained in colourless, flat, pointed needles, showing straight extinction and melting, with decomposition, at 255—256°. The yield was 7 grams, and more could be obtained by diluting the acetic anhydride mother liquor with water.

The substance is extraordinarily difficult to burn, and we preferred to determine the carbon and hydrogen in separate portions, using lead chromate for the former and copper oxide for the latter.

0·1838 gave 0·4662 CO_2. C = 69·17.
0·1970 „ 0·4988 CO_2. C = 69·05.
0·1623 „ 0·0617 H_2O. H = 4·22.
0·1568 „ 0·0584 H_2O. H = 4·13.
0·2290 „ 16 c.c. moist nitrogen at 11° and 742·4 mm. N = 8·13.
$C_{20}H_{14}O_4N_2$ requires C = 69·36 ; H = 4·04 ; N = 8·08 per cent.

The compound is therefore the *diacetyl* derivative of acicular phenanthraquinonedihydrocyanide :

$$\begin{array}{l} C_6H_4\cdot C(O\cdot C_2H_3O)\cdot CN \\ | \qquad\quad | \\ C_6H_4\cdot C(O\cdot C_2H_3O)\cdot CN \end{array}.$$

Laminar Phenanthraquinonedihydrocyanide.—In the course of an attempt to prepare Japp and Miller's acicular phenanthraquinonedihydrocyanide we employed a much stronger hydrocyanic acid than the 30 per cent. aqueous solution prescribed by them. As very little reaction took place in the cold we heated the mixture of phenanthraquinone and hydrocyanic acid in a stout, corked flask. Most of the phenanthraquinone dissolved, and the solution, on cooling, deposited laminæ, quite different in appearance from the needles of Japp and Miller's compound, and having a much higher decomposing point. The filtrate from the laminæ, as it gave off hydrocyanic acid by exposure to the air, deposited a large quantity of the acicular compound. After various experiments we found that the laminar modification could be best prepared by the following method.

Five grams of finely-powdered phenanthraquinone and 5 grams of anhydrous hydrocyanic acid were heated for 5 hours at 60° in a strong glass tube, of test-tube form and closed by an india-rubber stopper tightly wired. The tube was clamped upright so that only the extreme lower end dipped into a beaker of water heated to the required temperature. In this way a circulation and reflux distillation of the liquid was kept up, and the phenanthraquinone went into solution. On cooling, the liquid deposited colourless, elongated, six-sided laminæ, with bevelled edges, also thick short prisms, of the new compound. After standing for six days in the cold the liquid was decanted from the crystals, which were then washed with 85 per cent. hydrocyanic acid and dried in a vacuum desiccator over sulphuric acid. As the crystals turned brownish on the surface in drying they were washed with chloroform to remove the regenerated phenanthraquinone. The powdered substance dissolved, although with greater difficulty than the acicular modification, in hot benzene, and was deposited in slender, oblique prisms, showing straight extinction. The elongated, six-sided laminæ extinguish at an angle of about 25° from the long axis. When heated, the substance did not decompose until 160—170° (very much higher than the acicular modification), turning red and giving off gas, and finally melting at 200°, the melting point of phenanthraquinone. The original laminæ and thick, short prisms, on the one hand, and the slender prisms from benzene on the other, showed an absolutely identical behaviour in this respect, and all gave the same diacetyl derivative (see next section).

Analysis showed that the compound had the composition of a *phenanthraquinonedihydrocyanide*, $\begin{array}{l} C_6H_4\cdot C(OH)\cdot CN \\ | \qquad\quad | \\ C_6H_4\cdot C(OH)\cdot CN \end{array}$. It is stereoisomeric with the acicular modification.

0·1559 gave 0·4162 CO_2 and 0·0554 H_2O. C = 72·81 ; H = 3·94.
0·1842 „ 16·4 c.c. moist nitrogen at 10° and 762 mm. N = 10·69.
0·1850 „ 17 c c. moist nitrogen at 14° and 750 mm. N = 10·66.
$C_{16}H_{10}O_2N_2$ requires C = 73·28 ; H = 3 82 ; N = 10·69 per cent.

Analyses I and II were made with the original substance merely washed with chloroform ; analysis III with the substance purified by recrystallisation from benzene.

Both the phenanthraquinonedihydrocyanides are slowly decomposed by the moisture of the air and rapidly on boiling with water or with alcohol. The latter solvent readily dissolves them with evolution of hydrocyanic acid and formation of phenanthraquinone. This decomposition, however, does not occur if the water or the alcohol contains hydrochloric acid.

Acetylation of Laminar Phenanthraquinonedihydrocyanide.—The re-

action was carried out as in the case of the acicular compound (*vide supra*) using the same quantities. The yield of uncrystallised substance was 11 grams. It was deposited from hot glacial acetic acid in long, flat, pointed needles, showing straight extinction, and melting, with decomposition, at 235—237°. It is difficult to burn, and the carbon was determined separately by combustion of the substance in a current of moist oxygen. The figures agreed with the formula of a *diacetyl* derivative, $\begin{array}{l} C_6H_4 \cdot C(O \cdot C_2H_3O) \cdot CN \\ | \quad\quad\; | \\ C_6H_4 \cdot C(O \cdot C_2H_3O) \cdot CN \end{array}$.

0·1549 gave 0·3946 CO_2. C = 69·47.
0·1664 „ 0·0628 H_2O. H = 4·19.
0·2032 „ 14 c.c. moist nitrogen at 9° and 760·5 mm. N = 8·23.
$C_{20}H_{14}O_4N_2$ requires C = 69·36 ; H = 4·04 ; N = 8·08 per cent.

The diacetyl derivatives of acicular and laminar phenanthraquinonedihydrocyanide are indistinguishable in appearance and optical properties, so far at least as a rough examination in polarised light is able to decide; but the former melts at 255—256°, the latter at 235—237°, and the mixture of the two at about 220°—in every case with decomposition.

Hydrolysis of the Phenanthraquinonedihydrocyanides.

Hydrolysis of Acicular Phenanthraquinonedihydrocyanide.—Japp and Miller (*loc. cit.*) showed that carbon dioxide is evolved during the formation of phenanthranil and hydroxydihydrophenanthranil by the hydrolysis of acicular phenanthraquinonedihydrocyanide with cold, fuming hydrochloric acid :—

$$C_{16}H_{10}O_2N_2 + H_2O = \underset{\text{Phenanthranil.}}{C_{15}H_9ON} + CO_2 + NH_3,$$

and

$$C_{16}H_{10}O_2N_2 + 2H_2O = \underset{\text{Hydroxydihydrophenanthranil.}}{C_{15}H_{11}O_2N} + CO_2 + NH_3.$$

As, therefore, the evolution of carbon dioxide may be utilised as an index of the progress of the reaction, we attached, in the majority of the experiments which we made, a delivery tube to the flask in which the hydrolysis was carried out, and collected the carbon dioxide from time to time.

In our first hydrolysis experiment the acicular phenanthraquinonedihydrocyanide, prepared as already described *and dried over sulphuric acid*, was mixed with an excess of the strongest hydrochloric acid and allowed to stand at the ordinary temperature for a fortnight. No gas was given off, and the substance in the flask, freed from hydro-

chloric acid, proved to be unchanged dihydrocyanide. We therefore reverted to Japp and Miller's method, which we describe in detail, inasmuch as the results which we obtained differed somewhat from theirs.

The freshly-prepared hydrocyanide, freed as far as possible from adhering aqueous hydrocyanic acid by means of the filter-pump, *but still moist with this liquid*, was mixed with a large excess of the strongest hydrochloric acid (the ordinary fuming acid into which hydrogen chloride had been passed to complete saturation) in a flask fitted with a delivery tube. Carbon dioxide was evolved and was collected over mercury in a tube containing a little water so as to absorb any hydrogen chloride. Japp and Miller state that the evolution of carbon dioxide ceases "after some days." This is incorrect. The evolution became much slower after about a week, but did not entirely cease until $3\frac{1}{2}$ months had elapsed. The contents of the flask were then diluted with water, and the solid matter was separated by filtration, digested several times on the water-bath with sodium carbonate, and filtered hot. (Too long digestion is to be avoided, as otherwise the sodium salt of hydroxydihydrophenanthranil is decomposed with separation of a brown substance.) After the treatment with sodium carbonate, there was only a small residue which proved to be *diphenylenetartramide* (*vide infra*), whereas Japp and Miller found a large insoluble residue of phenanthraquinone, which must have been regenerated by the action of the hot aqueous carbonate solution on the acicular phenanthraquinonedihydrocyanide that had escaped hydrolysis owing to the shortness of the time during which the experiment was allowed to proceed.*

The united sodium carbonate extracts yielded, on acidification, a copious precipitate, which, after recrystallisation from boiling benzene, was obtained in tufts of slender needles of *hydroxydihydrophenanthranil*, $\begin{array}{l} C_6H_4\cdot C(OH)\cdot CO \\ \vert \qquad\quad \vert \qquad\quad\ \vert \\ C_6H_4\cdot CH - NH \end{array}$, melting at 183°. A small quantity of *phenanthranil*, $\begin{array}{l} C_6H_4\cdot C\cdot CO \\ \vert \qquad \Vert \quad \vert \\ C_6H_4\cdot C\cdot NH \end{array}$ (m. p. 241°), was obtained from the benzene mother liquor and was freed from any hydroxydihydrophenanthranil with which it was mixed by dissolving it in sodium carbonate and digesting the solution for some days on the water-bath, by which treatment the salt of hydroxydihydrophenanthranil is destroyed with separation of a brown insoluble substance. The filtrate then gives, on acidifying, a precipitate of pure phenanthranil (compare Japp and Miller, *loc. cit.*, p. 36).

Although acicular phenanthraquinonedihydrocyanide that has been

* This residue is not referred to in the original paper.—F. R. J.

previously dried is not hydrolysed by hydrochloric acid in the cold, the reaction readily takes place at a higher temperature.

Seven grams of dry acicular phenanthraquinonedihydrocyanide and 150 c.c. of ordinary fuming hydrochloric acid were heated for 40 hours at 80—90° in a flask fitted with an air condensing tube. The product of the reaction was treated precisely as in the previous experiment; but in the present case phenanthranil was the chief product. It separated in a state of purity from the benzene solution, whilst hydroxydihydrophenanthranil, mixed with phenanthranil, was obtained from the mother liquor.

In this way, by varying the temperature at which the hydrolysis is conducted, one can obtain either phenanthranil or hydroxydihydrophenanthranil as chief product.

Japp and Miller state that phenanthranil and hydroxydihydrophenanthranil are of about equal solubility in benzene. We find, however, that the latter is the more soluble.

We also studied the action of alcoholic hydrogen chloride on acicular phenanthraquinonedihydrocyanide and obtained, in addition to the foregoing compounds, the ethyl ester of phenanthranilic acid and an ethyl derivative of hydroxydihydrophenanthranil.

Twenty-four grams of dry acicular phenanthraquinonedihydrocyanide were mixed with 300 grams of saturated alcoholic hydrogen chloride, and the mixture was allowed to stand for 3 months in a flask fitted with a mercury safety valve. It was noticed that less carbon dioxide was evolved than when aqueous hydrochloric acid was used. The solid substance was separated by filtration, and the alcoholic filtrate was diluted with an equal bulk of water. The solid was treated with water to remove ammonium chloride, and the residue was treated several times with boiling benzene, which extracted phenanthranil mixed with a little hydroxydihydrophenanthranil. The residue from the extraction with benzene was recrystallised from boiling glacial acetic acid, in which it readily dissolved; the crystals were again extracted with benzene, and the residue again recrystallised from glacial acetic acid. The substance was thus obtained in slender transparent prisms melting with decomposition at 274°. It proved to be *diphenylenetartramide* combined with a molecule of acetic acid, the latter being present either as solvent of crystallisation or as salt-forming acid, but probably the former, owing to the ease with which the acetic acid was expelled on heating the compound, and also owing to the fact that the diphenylenetartramide was not found combined with hydrochloric acid in the process in which it was formed. The yield was 0·8 gram. The compound was analysed before we discovered that it contained acetic acid.

0·2040 gave 0·4512 CO_2 and 0·0924 H_2O. C = 60·32 ; H = 5·03.
0·2118 ,, 13·65 c.c. moist nitrogen at 9° and 764·5 mm. N = 7·79.
$C_{16}H_{14}O_4N_2,C_2H_4O_2$ requires C = 60·33 ; H = 5·02 ; N = 7·82 per cent.

The compound was heated at 110° until its weight was constant. It lost 1 mol. proportion of acetic acid.

0·3222 lost, at 110°, 0·0546. Acetic acid = 16·94.
$C_{16}H_{14}O_4N_2,C_2H_4O_2$ requires acetic acid = 16·76 per cent.

The residue melted with decomposition at 274°, like the original substance, as the latter had of course parted with its acetic acid of crystallisation far below this temperature. It was analysed.

0·1342 gave 0·3164 CO_2 and 0·0570 H_2O. C = 64·30 ; H = 4·71.
0·1241 ,, 10·05 c.c. moist nitrogen at 7·5° and 746 mm. N = 9·62.
$C_{16}H_{14}O_4N_2$ requires C = 64·42 ; H = 4·69 ; N = 9·39 per cent.

The compound is, therefore, *diphenylenetartramide*,

$$\begin{array}{l} C_6H_4\cdot C(OH)\cdot CONH_2 \\ | \qquad\quad | \\ C_6H_4\cdot C(OH)\cdot CONH_2 \end{array}.$$

It is identical with the product obtained by the action of cold fuming hydrochloric acid on acicular phenanthraquinonedihydrocyanide (*vide supra*), as was proved by a comparison of the two specimens and by the mixture melting-point test.

Diphenylenetartramide is not chemically altered by heating with fuming hydrochloric acid at 190—200°, as it merely dissolves in the hot acid and crystallises out again on cooling. It is therefore evident that it cannot be an intermediate product in the formation of phenanthranil and hydroxydihydrophenanthranil.

The phenanthranil obtained by the extraction of the original residue with benzene was freed from hydroxydihydrophenanthranil by destroying the latter compound by digesting the mixture with sodium carbonate for several days on the water-bath as described in the case of the product of the hydrolysis with aqueous hydrochloric acid. It gave the correct melting point of 241°, and was further identified by the mixture melting-point test.

The alcoholic hydrogen chloride filtrate, diluted as already mentioned with water, deposited a solid substance. This was separated by filtration, washed with water, and extracted with hot sodium carbonate, which removed a quantity of hydroxydihydrophenanthranil, which on reprecipitation and recrystallisation from benzene melted at 183°, and was further identified by the mixture melting-point test.

The residue from the foregoing sodium carbonate extraction, recrystallised from benzene, formed very slender white needles melting at 207°. The yield was 0·7 gram.

0·1666 gave 0·4680 CO_2 and 0·0854 H_2O. C = 76·61 ; H = 5·69.
0·2048 ,, 9·05 c.c. moist nitrogen at 6° and 741 mm. N = 5·24.
$C_{17}H_{15}O_2N$ requires C = 76·98 ; H = 5·66 ; N = 5·28 per cent.

The synthesis of this compound, to be described later on, from the sodium salt of hydroxydihydrophenanthranil and ethyl iodide, and the fact that it is not hydrolysed by boiling it with alcoholic potassium hydroxide, lead us to regard it as a *hydroxyethyldihydrophenanthranil*, $\begin{matrix} C_6H_4\cdot C(OH)\cdot CO \\ C_6H_4\cdot CH \text{---} N\cdot C_2H_5 \end{matrix}$, in which the ethyl group is attached to nitrogen. Possibly the sodium salt of hydroxydihydrophenanthranil is derived from the tautomeric form and has the formula, $\begin{matrix} C_6H_4\cdot C(OH)\cdot C\cdot ONa \\ C_6H_4\cdot CH \text{---} N \end{matrix}$, or possibly the side chain opens in the formation of this salt, as in the case of the metallic salts of phenanthranil. Japp and Miller were unable to obtain the metallic salts of hydroxydihydrophenanthranil sufficiently pure to decide with certainty on their composition.

The dilute alcoholic hydrochloric acid filtrate, from which the foregoing substance had been separated by filtration, was allowed to evaporate spontaneously. As the alcohol was given off, a brownish solid was deposited ; this was boiled with benzene, which did not dissolve it, but left it white. This white substance proved to be the hydrochloride of a weak base ; it was found that, by digesting it with water on the water-bath for half an hour, the whole of the hydrochloric acid could be removed. The basic product resulting from this treatment was recrystallised first from alcohol and afterwards from benzene ; from the latter solvent it is deposited in slender needles with a yellowish tinge, melting at 185°, with decomposition, to a red liquid which resolidifies and then does not melt even at 290°.

0·1485 gave 0·4171 CO_2 and 0·0742 H_2O. C = 76·60 ; H = 5·55.
0·1868 ,, 8·45 c.c. moist nitrogen at 9° and 733 mm. N = 5·24.
$C_{17}H_{15}O_2N$ requires C = 76·98 ; H = 5·66 ; N = 5·28 per cent.

We regard this compound as *ethyl phenanthranilate* (10-*aminophenanthrene-9-carboxylate*), $\begin{matrix} C_6H_4\cdot C\cdot CO_2C_2H_5 \\ C_6H_4\cdot C\cdot NH_2 \end{matrix}$, although we must point out that the fact that the substance does not interact with benzaldehyde, even at the boiling point of the latter, is not in keeping with this formula.

When the foregoing ester (m. p. 185°) is heated with aqueous caustic soda, it dissolves, and on acidifying the solution, phenanthranil is precipitated, the liberated phenanthranilic acid parting with water and yielding this compound. The phenanthranil thus obtained was recrystallised from benzene. It showed the correct melting point of 241° and was further identified by the mixture melting-point test.

By treating the foregoing ester (m. p. 185°) in the cold with excess of acetic anhydride containing a little concentrated sulphuric acid (1 drop per 5 grams), a crystalline substance was obtained, insoluble in the ordinary organic menstrua, melting at 218—219°, and yielding, on analysis, C = 76·55, H = 4·47, N = 5·05. These figures do not appear to lead to any formula that can be accounted for. Possibly the carbon is too low, but we had not sufficient substance for further analysis.

An attempt to synthesise the foregoing ester (m. p. 185°) from sodium phenanthranilate and ethyl iodide yielded, instead, *phenanthranil ethyl ester*, $\begin{array}{l} C_6H_4\cdot C\cdot C\cdot OC_2H_5 \\ C_6H_4\cdot C\cdot N \end{array}$ (m. p. 110°), derived from the lactim form of phenanthranil (*vide infra*).

Hydrolysis of Laminar Phenanthraquinonedihydrocyanide.—In the case of this substance only the hydrolysis with aqueous hydrochloric acid was studied. At the ordinary temperature fuming hydrochloric acid had no action whatever. It was necessary to heat the finely-powdered substance with the fuming acid at 100° in order to obtain any result. Only a small quantity of *phenanthranil* and *hydroxydihydrophenanthranil* could be isolated from the product. Dark-coloured, resinous matters, insoluble in sodium carbonate, were formed in considerable amount.

Hydroxydihydrophenanthranil,

$$\begin{array}{l} C_6H_4\cdot C(OH)\cdot CO \\ C_6H_4\cdot CH\text{---}NH \end{array} \quad \text{or} \quad \begin{array}{l} C_6H_4\cdot C(OH)\cdot C\cdot OH \\ C_6H_4\cdot CH\text{---}N \end{array} \quad \text{(m. p. 183°).}$$

Acetylhydroxydihydrophenanthranil, $\begin{array}{l} C_6H_4\cdot C(OH)\cdot CO \\ C_6H_4\cdot CH\text{---}N\cdot C_2H_3O \end{array}$ (m. p. 190—192°, with decomposition).—One gram of hydroxydihydrophenanthranil, 6 grams of acetic anhydride, and 1 drop of concentrated sulphuric acid were allowed to interact in the cold for 3 weeks. The solid was filtered off, washed with a little cold glacial acetic acid, and recrystallised from boiling alcohol. It forms small white needles melting at 190—192° with decomposition. The yield was almost 1 gram.

0·1826 gave 0·4904 CO_2 and 0·0792 H_2O. C = 73·24 ; H = 4·81.
0·1460 ,, 6·2 c.c. moist nitrogen at 6° and 751 mm. N = 5·10.
$C_{17}H_{13}O_3N$ requires C = 73·11 ; H = 4·65 ; N = 5·01 per cent.

The compound is therefore a *monacetyl* derivative of hydroxydihydrophenanthranil. The acetyl group replaces the labile hydrogen atom, as the compound does not dissolve in sodium carbonate. On long digestion with sodium carbonate solution on the water-bath, however, it is decomposed with separation of the brown amorphous substance which hydroxydihydrophenanthranil yields under similar

circumstances, the decomposition being, in the present case, doubtless preceded by the hydrolysis of the acetyl derivative.

Benzylidenehydroxydihydrophenanthranil,

$$\begin{array}{l} \qquad\qquad\quad CH{\cdot}C_6H_5 \\ \qquad\qquad\quad O \quad\; O \\ C_6H_4{\cdot}C{-\!-}C \\ C_6H_4{\cdot}CH{\cdot}N \end{array}$$

(m. p. 245—246° with decomposition).—Half a gram of hydroxydihydrophenanthranil was boiled for 3 minutes in a test-tube with 2 grams of benzaldehyde. Water was given off. Alcohol was then added and the mixture digested for some time. The crystalline substance which separated was recrystallised from boiling glacial acetic acid, from which it was deposited in clusters of very slender white needles melting at 245—246° with decomposition, evolving gas and turning yellow. It is very sparingly soluble in alcohol and in benzene, and does not dissolve in sodium carbonate or sodium hydroxide even on long heating.

0·1702 gave 0·5018 CO_2 and 0·0728 H_2O. C = 80·40; H = 4·75.
0·2585 „ 9·35 c.c. moist nitrogen at 7° and 756 mm. N = 4·36.
$C_{22}H_{15}O_2N$ requires C = 81·23; H = 4·61; N = 4·30 per cent.

The compound is thus the *benzylidene* derivative of hydroxydihydrophenanthranil.

Phenanthranil, on the contrary, is not acted on by benzaldehyde at the boiling point of the latter.

Synthesis of Hydroxyethyldihydrophenanthranil,

$$\begin{array}{l} C_6H_4{\cdot}C(OH){\cdot}CO \\ C_6H_4{\cdot}CH{-\!-\!-}N{\cdot}C_2H_5 \end{array}$$

(m. p. 207°).—As the salts of hydroxydihydrophenanthranil are very unstable, we thought it better, instead of attempting to prepare its sodium salt and acting on this with ethyl iodide, to employ the method of alkylation devised by Japp and Klingemann (Trans., 1888, **53**, 526—527) to meet such cases.

One and a half grams of hydroxydihydrophenanthranil and 4·8 grams of ethyl iodide were dissolved in absolute ethyl alcohol, the solution was boiled in a flask fitted with a reflux condenser, and a solution of 0·7 gram of sodium in absolute alcohol was allowed to fall drop by drop into the boiling liquid. The boiling was continued for $3\frac{1}{2}$ hours. The solution was cooled, diluted with water, and extracted with ether. The ethereal extract was freed from a small quantity of unchanged hydroxydihydrophenanthranil by shaking it with sodium carbonate solution, and a further quantity of the same compound was precipitated on acidifying the extracted aqueous alcoholic solution, 0·4 gram of unchanged substance in all being thus recovered. The ethereal extract yielded, on evaporation, *hydroxy-*

ethyldihydrophenanthranil, which crystallised from boiling benzene in slender, white needles melting at 207°. It was proved by the mixture melting-point test to be identical with the substance of the same melting point obtained by the action of alcoholic hydrogen chloride on acicular phenanthraquinonedihydrocyanide.

0·2000 gave 0·5633 CO_2 and 0·1029 H_2O. C = 76·77 ; H = 5·71.
$C_{17}H_{15}O_2N$ requires C = 76·98 ; H = 5·66.

As already mentioned, the compound is not hydrolysed by boiling it with alcoholic potassium hydroxide. We also ascertained that boiling benzaldehyde is without action on it.

Acetyl Derivative of Hydroxyethyldihydrophenanthranil,

$$\begin{array}{l} C_6H_4\cdot C(O\cdot C_2H_3O)\cdot CO \\ C_6H_4\cdot CH\text{———}N\cdot C_2H_5 \end{array}$$

(m. p. 148—149°).—One gram of hydroxyethyldihydrophenanthranil (m. p. 207°), 10 grams of acetic anhydride, and 1 drop of concentrated sulphuric acid were allowed to stand in the cold. At first the substance dissolved, but afterwards the liquid became filled with crystals. At the end of a fortnight the solid was separated by filtration; the filtrate, diluted with water, yielded a further quantity of the same product, the total yield being 0·8 gram. The substance was purified by dissolving it in benzene and adding light petroleum, when it separates in very slender, silky needles melting constantly at 148—149°.

0·1674 gave 0·4548 CO_2 and 0·0847 H_2O. C = 74·09 ; H = 5·62.
0·2544 „ 10·00 c.c. moist nitrogen at 15·5° and 756 mm. N = 4·56.
$C_{19}H_{17}O_3N$ requires C = 74·26 ; H = 5·53 ; N = 4·56 per cent.

Hydrolysis of Hydroxydihydrophenanthranil with Fuming Hydrochloric Acid.—Three sealed tubes, each containing 2 grams of hydroxydihydrophenanthranil with 50 c.c. of fuming hydrochloric acid, were heated for 6 hours at 130°. There was pressure in the tubes on opening. The fused mass of organic substance was powdered and extracted with ether. The ethereal solution was shaken with dilute sodium hydroxide, and the sodium hydroxide solution, heated to expel ether and then filtered, was saturated with carbon dioxide. A phenolic substance was thus precipitated which, after recrystallisation from hot benzene, formed brownish needles melting at 151—153°. The properties were those of 9-*hydroxyphenanthrene*, $\begin{array}{l} C_6H_4\cdot CH \\ C_6H_4\cdot C\cdot OH \end{array}$, and its melting point was not altered by mixing it with a specimen of this compound prepared by Japp and Klingemann (Trans., 1893, **63**, 770) by the partial reduction of phenanthraquinone with hydriodic acid.

0·1601 gave 0·5051 CO_2 and 0·0751 H_2O. C = 86·04; H = 5·21.
$C_{14}H_{10}O$ requires C = 86·60; H = 5·16 per cent.

It was further identified by mixing its hot benzene solution with a similar solution of phenanthraquinone. The mixed solution deposited, on cooling, ruby-red, lozenge-shaped crystals of the compound $C_{28}H_{18}O_3$, melting at 155° (compare Japp and Findlay, 1897, **71**, 1121).

The ethereal solution from which the 9-hydroxyphenanthrene had been removed by sodium hydroxide yielded, on evaporation, a substance, which, after recrystallisation from benzene, formed crystals melting at 209°. This proved to be *9-phenanthryl oxide*,

$$\begin{matrix} C_6H_4\cdot CH & HC\cdot C_6H_4 \\ | \quad\quad \| & \| \quad\quad | \\ C_6H_4\cdot C{-}O{-}C\cdot C_6H_4 & \end{matrix}$$

(m. p. 210°).

It was identified by a comparison, including the mixture melting-point test, with the original specimen of this substance prepared by Japp and Findlay (*loc. cit.*, p. 1119). Examined microscopically, both specimens appeared as rhomboidal plates with an acute angle of about 66° and with extinction parallel to the diagonal.

The residue, which remained after the extraction of the original product of hydrolysis with ether, was recrystallised from boiling coal oil (b. p. 170—190°). It was thus obtained in clusters of colourless slender needles melting at 305° and was identified as *tetraphenylene-furfuran*,

$$\begin{matrix} C_6H_4\cdot C & {-}{-} & C\cdot C_6H_4 \\ | \quad\quad \| & & \| \quad\quad | \\ C_6H_4\cdot C & & C\cdot C_6H_4 \\ & \diagdown \; \diagup & \\ & O & \end{matrix}$$

both by the mixture melting-point test and by the colour reaction with concentrated sulphuric acid and sodium nitrite (compare Japp and Findlay, *loc. cit.*, p. 1120).

Phenanthranil,

$$\begin{matrix} C_6H_4\cdot C\cdot CO \\ | \quad\quad \| \quad | \\ C_6H_4\cdot C\cdot NH \end{matrix}, \text{ or } \begin{matrix} C_6H_4\cdot C\cdot C\cdot OH \\ | \quad\quad \| \quad \| \\ C_6H_4\cdot C\cdot N \end{matrix} \quad \text{(m. p. 241°).}$$

Acetylphenanthranil, $\begin{matrix} C_6H_4\cdot C\cdot CO \\ | \quad\quad \| \quad | \\ C_6H_4\cdot C\cdot N\cdot C_2H_3O \end{matrix}$ (m. p. 145°).—The acetylation was carried out with acetic anhydride containing a small quantity of concentrated sulphuric acid, exactly as in the acetylation of hydroxydihydrophenanthranil (*vide supra*) and using the same proportions. The product was crystallised from hot alcohol, in which it is readily soluble. It formed clusters of slender, silky needles melting at 145°. It does not dissolve in sodium carbonate solution, even at 100°. Analysis showed that a *monacetyl* derivative had been formed.

0·1634 gave 0·4660 CO_2 and 0·0624 H_2O. C = 77·77 ; H = 4·24.
0·1716 „ 0·4930 CO_2 „ 0·0666 H_2O. C = 78·35 ; H = 4·31.
0·2186 „ 9·05 c.c. moist nitrogen at 6° and 759 mm. N = 5·03.
$C_{17}H_{11}O_2N$ requires C = 78·16 ; H = 4·21 ; N = 5·36 per cent.

Lactim Ester of Phenanthranil (*Phenanthranil Ethyl Ester*),

$$\begin{array}{l} C_6H_4\cdot C\cdot C\cdot OC_2H_5 \\ C_6H_4\cdot C\cdot N \end{array}$$

(m. p. 110°).—Sodium phenanthranilate, $\begin{array}{l} C_6H_4\cdot C\cdot CO_2Na \\ C_6H_4\cdot C\cdot NH_2 \end{array}$,$4H_2O$, was prepared by dissolving phenanthranil in a hot solution of sodium carbona'e; on cooling, the liquid deposited laminæ of the salt. It was dried at 110° to expel water of crystallisation. The dried salt, together with an excess of ethyl iodide, was dissolved in absolute alcohol, and the mixture was boiled for 3½ hours. Dilution with water precipitated a white substance; this was filtered off and digested with warm sodium carbonate, which removed a little phenanthranil. The residue was recrystallised, first from alcohol and afterwards from light petroleum (sp. gr. 0·71—0·72). It was thus obtained in slender needles melting at 110°. It is very soluble both in alcohol and in benzene.

0·1342 gave 0·4064 CO_2 and 0·0662 H_2O. C = 82·59 ; H = 5·48.
0·2256 „ 11·25 c.c. moist nitrogen at 11·5° and 758 mm. N = 5·92.
$C_{17}H_{13}ON$ requires C = 82·59 ; H = 5·26 ; N = 5·66 per cent.

An attempt to acetylate the compound with acetic anhydride containing a little sulphuric acid gave no result.

A portion of the compound was digested on the water-bath in a silver basin with a 20 per cent. solution of potassium hydroxide in absolute alcohol, renewing the alcohol as required. The alcohol was then expelled, water was added, and the mixture was digested and filtered hot from the insoluble residue. The hot filtrate was acidified and the precipitate recrystallised from benzene. Needles of *phenanthranil* (m. p. 241°) were thus obtained. The insoluble residue, separated by filtration from the potassium hydroxide solution, was crystallised from benzene; it was thus obtained in slender needles melting at 207°, and was identical with the *hydroxyethyldihydrophenanthranil*, $\begin{array}{l} C_6H_4\cdot C(OH)\cdot CO \\ C_6H_4\cdot CH \text{——} N\cdot C_2H_5 \end{array}$, already described, as was proved by the mixture melting-point test. The lactim ester of phenanthranil is thus partly hydrolysed to phenanthranil, and partly transformed by migration of the ethyl group and assumption of the elements of water into hydroxyethyldihydrophenanthranil.

The latter result was so surprising that we repeated the entire

experiment, preparing the lactim ester of phenanthranil from a specimen of phenanthranil which had been purified by digesting it for several days on the water-bath with a solution of sodium carbonate and from which, consequently, every trace of hydroxydihydrophenanthranil must have been removed by the destruction of this compound. The result, however, was the same as before.

The only alternative, so far as we can see, to assuming a migration of the ethyl group from carbon to nitrogen in a portion of the lactim ester is to suppose that the latter substance is in reality a mixture of the *O*-ethyl and *N*-ethyl derivatives of phenanthranil, the former being hydrolysed by the caustic alkali to phenanthranil, and the latter taking up the elements of water to form the hydroxyethyldihydrophenanthranil. The lactim ester of phenanthranil, however, shows no sign of being other than a perfectly homogeneous substance.

We also digested a specimen of hydroxyethyldihydrophenanthranil (m. p. 207°), prepared from hydroxydihydrophenanthranil, ethyl iodide, and sodium ethoxide (*vide supra*), for 3½ hours with 20 per cent. alcoholic potassium hydroxide on the water-bath. The hydroxyethyldihydrophenanthranil was recovered unchanged, and the potash solution, treated as in the experiment just described, gave no precipitate on acidifying.

Hydrolysis of Phenanthranil with Fuming Hydrochloric Acid.—Unlike hydroxydihydrophenanthranil, phenanthranil is not acted on by fuming hydrochloric acid at 130°. At a temperature of 160—170°, however, 9-*hydroxyphenanthrene* was formed, and was identified by its properties and by the mixture melting-point test. As the quantity of phenanthranil which we could spare for the experiment was small, we did not search for the other products obtained from hydroxydihydrophenanthranil.

The production of 9-hydroxyphenanthrene, both from phenanthranil and from hydroxydihydrophenanthranil, is of importance, inasmuch as it proves, as already pointed out, that both these compounds contain the phenanthrene nucleus.

Distinction between Phenanthranil (m. p. 241°) *and Hydroxydihydrophenanthranil* (m. p. 183°).—Both phenanthranil and hydroxydihydrophenanthranil crystallise from benzene in slender needles, the former being the less soluble. The two substances are very similar in appearance. In addition to the melting points, the following differences may be noted. In polarised light the needles of phenanthranil show straight extinction; those of hydroxydihydrophenanthranil oblique extinction at an angle of about 13° from the long axis. Phenanthranil does not dissolve in cold concentrated sulphuric acid, but, on warm-

ing, dissolves slowly, yielding a grass-green solution. Hydroxy-dihydrophenanthranil dissolves in cold concentrated sulphuric acid giving a light yellow solution which is unaltered on warming.

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LXIX.—*A Condensation Product of Mandelonitrile.*

By Francis Robert Japp, F.R.S., and Joseph Knox, B.Sc., Carnegie Scholar in the University of Aberdeen.

By saturating a solution of mandelonitrile (benzaldehydecyanhydrin) in absolute ether with gaseous hydrogen chloride, Minovici (*Ber.*, 1899, **32**, 2206) obtained a yellow compound of the formula $C_{16}H_{12}ON_2$:—

$$2C_6H_5\cdot CH(OH)\cdot CN = C_{16}H_{12}ON_2 + H_2O.$$

Minovici found the melting point of this substance at 200—203°. It was not hydrolysed by heating either with potassium hydroxide or with hydrochloric acid. It formed an unstable hydrochloride, which was at once decomposed in contact with water or alcohol, liberating the base. The author suggests, as a possible constitution,

$$C_6H_5\cdot CH(CN)\cdot C(OH)(CN)\cdot C_6H_5,$$

but admits that this formula is not in keeping with the reactions of the compound.

Minovici has failed to notice that this compound is identical with a substance which Japp and Miller (Trans., 1887, **51**, 29) obtained, along with other products, by dissolving benzil in alcohol, adding a considerable excess of anhydrous hydrocyanic acid, and saturating the liquid with gaseous hydrogen chloride. They point out that the compound contains in its molecule an atom of oxygen less than benzil-dihydrocyanide :

$$C_{16}H_{12}O_2N_2 = C_{16}H_{12}ON_2 + O,$$

but they were unable to prepare the substance by the action of alcoholic hydrogen chloride on pure benzildihydrocyanide. They found the melting point at 196—197°. The yield was very small.

Minovici's reaction explains the mode of formation of this substance in the process described by Japp and Miller. Under the influence of the alcoholic hydrocyanic acid a portion of the benzil is converted into a mixture of benzaldehyde and ethyl benzoate (compare Michael and Palmer, *Amer. Chem. J.*, 1885, **7**, 189); and the benzaldehyde then

interacts with the hydrocyanic acid to form mandelonitrile, which is finally transformed by the hydrogen chloride into the compound $C_{16}H_{12}ON_2$, as in Minovici's reaction. The formation of ethyl benzoate was observed by Japp and Miller (*loc. cit.*).

A careful comparison of the substance obtained by Minovici's method with one of Japp and Miller's original preparations showed that the two were identical. We confirmed in both cases the melting point 196—197° given by Japp and Miller. Minovici gives 200—203°.

The reactions of the compound lead us to regard it as 3-*keto*-2 : 5-*diphenyl*-3 : 4-*dihydro*-1 : 4-*diazine*, formed according to the scheme

$$\begin{matrix} C\equiv N \\ | \\ C_6H_5\cdot CH\cdot OH \end{matrix} + \begin{matrix} HO\cdot HC\cdot C_6H_5 \\ | \\ N\equiv C \end{matrix} - H_2O = \begin{matrix} & N & \\ HC & & C\cdot C_6H_5 \\ \| & & | \\ C_6H_5\cdot C & & CO \\ & NH & \end{matrix}.$$

It is somewhat difficult to give an account of the precise mechanism of the process in which the substance is produced, and we therefore confine ourselves to stating the reaction in the foregoing summary form.

The ketonic formula appears more probable than the tautomeric enolic form, because the former accounts better for the facts (1) that the compound cannot be acetylated, and (2) that, when it is reduced with hydriodic acid, the oxygen atom is replaced by 2 atoms of hydrogen; whereas, if a hydroxyl group were replaced by a hydrogen atom, the resulting diazine would not be further reduced. As regards the latter point, Staedel and Kleinschmidt, it is true, claim to have reduced 2 : 5-diphenyl-1 : 4-diazine ("*iso*indole") by the action of hydriodic acid to a yellow, basic compound (*Ber.*, 1878, **11**, 1746); but we have entirely failed to confirm this result (*vide infra*).

We find that when the condensation compound is distilled with zinc dust, it is reduced to 2 : 5-*diphenyl*-1 : 4-*diazine*,

$$\begin{matrix} & N & \\ HC & & C\cdot C_6H_5 \\ \| & & | \\ C_6H_5\cdot C & & CH \\ & N & \end{matrix}$$

(m. p. 194—195°), a compound first obtained by Staedel and Rügheimer by the action of ammonia on ω-chloroacetophenone (*Ber.*, 1876, **9**, 563), but of which the correct composition and constitution were ascertained later by L. Wolff (*Ber.*, 1887, **20**, 432).*

* Wolff, however, in accordance with the view at that time prevailing on the subject of the constitution of diazines of this type, formulated the compound with a para-bond between the two nitrogen atoms.

If, on the other hand, the condensation compound is reduced by heating it with hydriodic acid and red phosphorus, it yields a compound of the formula $C_{16}H_{14}N_2$ (m. p. 162—163°), which we regard as 2 : 5-*diphenyl*-3 : 4-*dihydro*-1 : 4-*diazine*,

```
          N
         / \
       HC   C·C6H5
       ||   |
  C6H5·C    CH2
         \ /
          NH
```

That it is not a 1 : 4-dihydro-compound is indicated by the fact that on distillation it does not part with hydrogen yielding 2 : 5-diphenyl-1 : 4-diazine. We were unable to acetylate this substance.

Of the numerous reactions which we tried with the condensation product, only the two foregoing gave positive results.

Attempts to obtain the condensation product by acting on mandelonitrile with other dehydrating agents did not give the desired result. Thus acetic anhydride to which a few drops of sulphuric acid had been added converted mandelonitrile in the cold, with liberation of hydrocyanic acid, into a compound melting at 239—240° and having the formula $C_{27}H_{26}O_6N_2$. The yield of this substance is greatly increased by previously adding to the mandelonitrile half its molecular proportion of benzaldehyde. It is formed according to the equation :

$$2C_6H_5{\cdot}CH(OH){\cdot}CN + C_6H_5{\cdot}CHO + (C_2H_3O)_2O = C_{27}H_{26}O_6N_2,$$

and its constitution may be represented by the formula

$$C_6H_5{\cdot}CH[NH{\cdot}CO{\cdot}CH(O{\cdot}C_2H_3O){\cdot}C_6H_5]_2.$$

The reaction in which it is formed is thus analogous to that discovered by Hepp and Spiess (*Ber.*, 1876, 9, 1425) in which acetaldehyde and benzonitrile, under the influence of concentrated sulphuric acid, yield ethylidenedibenzamide, $CH_3{\cdot}CH(NH{\cdot}CO{\cdot}C_6H_5)_2$. Heated with water at 180° the compound $C_{27}H_{26}O_6N_2$ was hydrolysed, yielding benzaldehyde, mandelic acid and acetic acid.

Experimental.

3-*Keto*-2 : 5-*diphenyl*-3 : 4-*dihydro*-1 : 4-*diazine*,

```
          N
         / \
       HC   C·C6H5
       ||   |
  C6H5·C    CO
         \ /
          NH
```

(m. p. 196—197°).

Comparison of the Compound $C_{16}H_{12}ON_2$ *obtained by Minovici's Method with that described by Japp and Miller.*—We prepared a quantity of the compound $C_{16}H_{12}ON_2$ by Minovici's method of saturating

a solution of mandelonitrile in *absolute* ether with gaseous hydrogen chloride (*Ber.*, 1899, **32**, 2206). The product was purified by boiling it in alcoholic solution with animal charcoal and afterwards recrystallising it repeatedly from alcohol. It was compared with a specimen of the substance of the same formula prepared by Japp and Miller from benzil by the method already described.

Both preparations melted at 196—197°, and showed no depression of melting point when mixed. Both crystallised in flat, pointed, lustrous, yellow needles showing straight extinction. Both dissolved in concentrated sulphuric acid giving an orange-yellow coloration. They were therefore identical.

Both products had been previously analysed by their discoverers.

We have already given our reasons for assigning to the compound the constitution of a 3-*keto*-2 : 5-*diphenyl*-3 : 4-*dihydro*-1 : 4-*diazine.*

As, of the two methods for preparing the compound, that of Minovici is both the simpler and gives the better—although a far from satisfactory—yield, it was employed in obtaining the material required for the following reactions.

The compound could not be acetylated either by boiling it for several hours with excess of a mixture of acetic anhydride and anhydrous sodium acetate, or by allowing it to stand in the cold with acetic anhydride containing a few drops of concentrated sulphuric acid, nor did it yield a nitroso-derivative on adding solid sodium nitrite to its solution in glacial acetic acid.

Distillation of the Compound $C_{16}H_{12}ON_2$ (m. p. 196—197°) *with Zinc Dust: Formation of* 2 : 5-*Diphenyl*-1 : 4-*diazine*,

$$\begin{array}{ccc} & N & \\ HC & & C\cdot C_6H_5 \\ C_6H_5\cdot C & & CH \\ & N & \end{array}.$$

—Eight grams of the compound $C_{16}H_{12}ON_2$ were distilled with zinc dust in four portions—2 grams of substance mixed with 20 grams of zinc dust being used for each distillation. The united alcoholic extracts of the distillates were concentrated, and the solution was nucleated with a trace of dust of 2 : 5-diphenyl-1 : 4-diazine, prepared by the action of alcoholic ammonia on ω-bromoacetophenone (Staedel and Kleinschmidt, *Ber.*, 1880, **13**, 836; compare also Braun and Victor Meyer, *Ber.*, 1888, **21**, 1279). The impure crystalline substance which was thus deposited was washed with cold ether and recrystallised thrice from boiling alcohol. It melted constantly at 194—195°. The quantity was unfortunately too small for analysis, but, as the properties of the substance pointed to its being 2 : 5-diphenyl-1 : 4-diazine, we identified it by comparison with a specimen of the latter

compound prepared by Staedel and Kleinschmidt's method just referred to. Both preparations consisted of yellow, lustrous crystals, which, under the microscope, appeared as broad, flat, pointed prisms showing straight extinction, or four-sided plates, frequently overlapping, extinguishing parallel to the diagonal. Both melted at 194—195°, and, when mixed together, showed no depression of melting point. Both dissolved in concentrated sulphuric acid with a reddish-yellow colour, and were precipitated on diluting the solution with water.

The substance is therefore 2 : 5-*diphenyl*-1 : 4-*diazine*.

Reduction of the Compound $C_{16}H_{12}ON_2$ (m. p. 196—197°) *with Hydriodic Acid: Formation of* 2 : 5-*Diphenyl*-3 : 4-*dihydro*-1 : 4-*diazine*,

```
          N
        /   \
     HC      C·C6H5
     ||      |
C6H5·C       CH2
        \   /
          NH
```

.—Two grams of the compound $C_{16}H_{12}ON_2$, 20 grams of hydriodic acid (sp. gr. 1·7), and 0·5 gram of red phosphorus were heated in a sealed tube at 200° for 6 hours. There was great pressure on opening the tube, which contained a brittle black mass. The contents of the tube were diluted with water, the acid liquid was decanted, and the remaining black solid was shaken with ether, in which it entirely dissolved. The ethereal solution was shaken with an aqueous solution of sulphur dioxide, which caused the separation of a brown oil; this was run off; it solidified on standing. The solid was digested on the water-bath with a solution of sodium carbonate, and purified by crystallisation from benzene with the addition of light petroleum. It was thus obtained in slender, white needles melting at 162—163°. A further quantity of the same compound was obtained from the ethereal solution.

Analysis gave figures agreeing with the formula of 2 : 5-*diphenyl*-3 : 4-*dihydro*-1 : 4-*diazine* :—

0·1792 gave 0·5349 CO_2 and 0·0985 H_2O. C = 81·40 ; H = 6·10.
0·2569 „ 25·6 c.c. moist nitrogen at 13° and 770 mm. N = 11·94.
$C_{16}H_{14}N_2$ requires C = 82·05 ; H = 5·98 ; N = 11·96 per cent.

In a previous reduction experiment in which the same proportions were employed and the tube was also heated for 6 hours, but at a temperature of only 150°, there was obtained, along with the foregoing product, a substance which crystallised from benzene, on addition of light petroleum, in slender, white needles melting at 182—184°. It contained iodine, which was not removed on adding aqueous sodium hydroxide to an alcoholic solution of the substance. It was not further examined.

2 : 5-Diphenyl-3 : 4-dihydro-1 : 4-diazine was distilled under reduced pressure in the hope that it might part with hydrogen and yield 2 : 5-diphenyl-1 : 4-diazine; but only unchanged substance could be isolated from the distillate.

An attempt to acetylate it by allowing it to stand at the ordinary temperature with acetic anhydride to which a few drops of sulphuric acid had been added, also led to no result. The substance was recovered unchanged.

Attempt to reduce 2 : 5-*Diphenyl*-1 : 4-*diazine*.—Staedel and Kleinschmidt (*Ber.*, 1878, **11**, 1746) state that "*iso*indole" (2 : 5-diphenyl-1 : 4-diazine) can be reduced with hydriodic acid to a yellow basic compound melting at 125° which yields an acetyl derivative crystallising in clear yellow needles melting at 190°. No analyses are given, and, so far as we can discover, nothing further has ever been published on the subject.

In view of the well-known difficulty of reducing paradiazines, we thought it of interest to test the correctness of the foregoing statements. We therefore heated 2 : 5-diphenyl-1 : 4-diazine (prepared by the action of alcoholic ammonia on ω-bromoacetophenone) with excess of hydriodic acid (sp. gr. 1·7) and red phosphorus for 6 hours at 200°. The tube contained a dark mass, from which we succeeded in isolating a very small quantity of a yellowish-brown, non-basic oil, which could not be induced to crystallise. Nearly the whole of the diazine was recovered unchanged.

Action of Acetic Anhydride containing a little Sulphuric Acid on a Mixture of Benzaldehyde and Mandelonitrile.—In the first experiment in which the substance about to be described was obtained, no benzaldehyde was added to the mixture, a part of the mandelonitrile breaking up in the process into benzaldehyde and hydrocyanic acid. By adding benzaldehyde to start with, the yield is greatly increased.

Ten grams of benzaldehyde and 25 grams of mandelonitrile were mixed and slowly added to 35 c.c. of acetic anhydride containing 7 drops of concentrated sulphuric acid. On standing for some time the mixture deposited slender needles, the quantity of which gradually increased. At the end of six weeks the mixture was poured into water and digested on the water-bath, first with water, then with a solution of sodium carbonate, and finally with a little alcohol. The white residue was then recrystallised from boiling glacial acetic acid, in which it is moderately soluble. It was thus obtained in slender, colourless needles, showing straight extinction and melting constantly at 239—240°. The substance has the constitution

$$C_6H_5\cdot CH[NH\cdot CO\cdot CH(O\cdot C_2H_3O)\cdot C_6H_5]_2.$$

0·1468 gave 0·3661 CO_2 and 0·0724 H_2O. C = 68·01 ; H = 5·48.
0·3102 „ 15·8 c.c. moist nitrogen at 15° and 768 mm. N = 6·03.
$C_{27}H_{26}O_6N_2$ requires C = 68·35 ; H = 5·48 ; N = 5·92 per cent.

A quantity of this substance was heated with water in a sealed tube at 180° for 8 hours. The organic products of hydrolysis were benzaldehyde, mandelic acid, and acetic acid. The benzaldehyde was identified by its smell, and by converting it into benzalazine (m. p. 93°); the mandelic acid by the mixture melting-point test; and the acetic acid by the ethyl acetate reaction.

We have to thank the Council of the Royal Society for an allotment from the Government Grant in aid of the work described in this and the two preceding papers.

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LXX.—*Action of Hydrazine on Unsaturated γ-Diketones.*

By Francis Robert Japp, F.R.S., and James Wood, M.A., B.Sc., Carnegie Scholar in the University of Aberdeen.

C. Paal and Heinrich Schulze (*Ber.*, 1900, **33**, 3796) have shown that the *cis*- and *trans*-forms of *s*-dibenzoylethylene,

$$C_6H_5·CO·CH{:}CH·CO·C_6H_5,$$

may be readily distinguished from one another by the greater ease with which the *cis*-form interacts with hydrazine to form a 1 : 2-diazine.

We have employed this reaction to ascertain the configurations of some analogous unsaturated γ-diketones: *αβ*-dibenzoylstyrene, dibenzoylstilbene, and *α*-benzoyl-*β*-trimethacetylstyrene. In the case of the last-mentioned compound, only one form is known; but the ease with which it forms a diazine shows that it has the *cis*-configuration. The result in the case of dibenzoylstyrene and dibenzoylstilbene has been to confirm the configurations assigned to the different modifications of these compounds by Japp and Klingemann (Trans., 1890, **57**, 667):

	cis-Form.	*trans*-Form.
αβ-Dibenzoylstyrene	m. p. 129°	m. p. 197—198°.
Dibenzoylstilbene	m. p. 220°	m. p. 232°.

The *cis*-forms of these compounds do not yield the corresponding diazines so readily as *cis*-*s*-dibenzoylethylene—doubtless owing to their

higher molecular weight and consequent greater inertness; and, for the same reason, their *trans*-forms do not interact with hydrazine at all, whereas *trans*-dibenzoylethylene differs from the *cis*-form, as already mentioned, only in the greater difficulty with which the formation of the diazine takes place. In the reactions which we are about to describe, a reducing action of the hydrazine sometimes accompanies the formation of the diazine, so that dibenzoylstyrene yields, at least when the reaction is allowed to take place in acetic acid solution, a mixture of the diazine with a dihydrodiazine; whilst, in the case of dibenzoylstilbene, a dihydrodiazine is the sole product. α-Benzoyl-β-trimethacetylstyrene, however, yields a diazine only.

EXPERIMENTAL.

Preparation of Dibenzoylstyrene, $\begin{matrix} C_6H_5\cdot C = CH \\ C_6H_5\cdot CO \quad CO\cdot C_6H_5 \end{matrix}$.—The *cis*-form of this compound, melting at 129°, is readily obtained by the method described by Japp and Klingemann (*loc. cit.*, p. 672) of warming a mixture of benzil and acetophenone with alcoholic potassium hydroxide containing a little water. Johannes Wislicenus and Lehmann (*Annalen*, 1898, **302**, 196), who had overlooked Japp and Klingemann's work, recommend the use of alcoholic sodium hydroxide (without the addition of water) as a condensing agent. This is quite the reverse of an improvement; for, according to the statements of these investigators, a further condensation of the dibenzoylstyrene with acetophenone to dibenzoyldiphenylbutadiene occurs under these conditions, and from the latter substance the dibenzoylstyrene has to be freed by recrystallisation.

We find that *iso*dibenzoylstyrene (m. p. 197—198°), the *trans*-form—which was obtained by Japp and Klingemann only in quantity sufficient for analysis, and that, too, under conditions that could not always be depended upon to yield the compound—is present in small but fairly constant amount in the dark-coloured, aqueous-alcoholic, alkaline filtrate from the *cis*-dibenzoylstyrene obtained in the initial process of condensation. If this filtrate is diluted with water, the tarry precipitate steam-distilled to remove unaltered acetophenone, the non-volatile residue dissolved in alcohol, the solution boiled with animal charcoal, concentrated, and allowed to stand, a small quantity of *trans*-dibenzoylstyrene is deposited in slender colourless needles (m. p. 197—198°). The yield is, however, so unsatisfactory that we were obliged to prepare large quantities of the *cis*-compound in order to obtain about 2 grams of its *trans*-isomeride.

Action of Hydrazine on Dibenzoylstyrene.—Dibenzoylstyrene (m. p. 129°) was mixed with 1 mol. proportion of a 50 per cent. solution of

hydrazine hydrate and heated in glacial acetic acid solution in an open flask on the water-bath for 15 minutes.

The experiment was repeated, using 2 mol. proportions of hydrazine hydrate.

In both cases the product, precipitated by water and crystallised either from alcohol or from benzene, consisted of a mixture of flat prisms or plates, which formed the chief product, with a small quantity of slender needles, the larger proportion of hydrazine hydrate giving a slightly improved yield of the latter compound. The two substances were separated by levigation with the mother liquor, the lighter needles being readily floated off.

The flat prisms or plates were purified by recrystallisation from benzene or alcohol. From the former solvent the substance was deposited in tables, from the latter in scales, melting at 170°. It was identical with Alexander Smith's 3 : 4 : 6-*triphenyl*-1 : 2-*diazine*,

```
            N
          //  \
$C_6H_5$·C     N
         |     ||
         C     C·$C_6H_5$
          \\  /
            C
            ·
          $C_6H_5$
```

(m. p. 171°, Smith), obtained by the oxidation of 3 : 4 : 6-triphenyl-1 : 2-dihydro-1 : 2-diazine (*Annalen*, 1896, **289**, 319), as we found by comparing our specimen with one prepared by Smith's method.

0·3427 gave 28·8 c.c. moist nitrogen at 10° and 759 mm. N = 9·00.
$C_{22}H_{16}N_2$ requires N = 9·09 per cent.

The needles were purified by recrystallisation, first from boiling alcohol and afterwards from glacial acetic acid. They were redeposited in slender, colourless needles, with a satiny lustre and melting at 181·5—182·5°, with decomposition, when rapidly heated. The crystals turned yellow on exposure to light.

0·1609 gave 0·5017 CO_2 and 0·0894 H_2O. C = 85·03 ; H = 6·17.
0·1903 „ 14·50 c.c. moist nitrogen at 13° and 758 mm. N = 8·98.
$C_{22}H_{18}N_2$ requires C = 85·16 ; H = 5·81 ; N = 9·03 per cent.

This is the formula of a 3 : 4 : 6-*triphenyldihydro*-1 : 2-*diazine*. The position of the two additive hydrogen atoms remains for the present undetermined. The substance is not identical with Alexander Smith's 3 : 4 : 6-triphenyl-1 : 2-dihydro-1 : 2-diazine (m. p. 186—188°, when quickly heated) (*Annalen*, 1896, **289**, 316), obtained by the interaction of desylacetophenone with hydrazine, a specimen of which we prepared for comparison. Smith's compound is of a bright yellow

colour, and was oxidised to 3 : 4 : 6-triphenyl-1 : 2-diazine in an attempt which we made to acetylate it by means of acetic anhydride containing a little concentrated sulphuric acid; in fact Smith had already oxidised it to this compound by treatment with chromium trioxide. Our isomeride, on the other hand, is colourless; an attempt to acetylate it yielded only a resinous mass; and we were quite unable to obtain the diazine from it by oxidation.

We afterwards found that by warming dibenzoylstyrene (m. p. 129°) with an excess of hydrazine in alcoholic (instead of acetic acid) solution on the water-bath for 15 minutes, an excellent yield of 3 : 4 : 6-triphenyl-1 : 2-diazine, without any admixture of the dihydro-compound, was obtained.

We also found that none of the dihydro-compound is formed when the diazine is boiled with hydrazine hydrate in acetic acid solution. In fact sodium in boiling alcohol has no action on the diazine. The reduction by hydrazine, to which the formation of the dihydro-compound is due, must, therefore, precede the condensation in which the diazine is formed.

The experiment was tried whether *iso*dibenzoylstyrene (m. p. 197—198°) would interact with hydrazine. After boiling the mixture in alcoholic solution for 6 hours, the *iso*-compound was recovered unchanged. *iso*Dibenzoylstyrene is therefore the *trans*-modification.

Action of Hydrazine on Dibenzoylstilbene, $\begin{matrix} C_6H_5\cdot C & = & C\cdot C_6H_5 \\ | & & | \\ C_6H_5\cdot CO & & CO\cdot C_6H_5 \end{matrix}$.—Dibenzoylstilbene (m. p. 220°), regarded by Japp and Klingemann (*loc. cit.*) as the *cis*-form, was obtained by Zinin by the oxidation of tetraphenylfurfuran ("lepiden") with nitric acid, and was termed by him "acicular oxylepiden." By heating it with alcoholic potassium hydroxide he converted it into the isomeric "octahedral oxylepiden" (m. p. 232°), which Japp and Klingemann formulate as *trans*-dibenzoylstilbene. That both these compounds are dibenzoylstilbenes is proved by the fact that, on reduction, they both yield tetraphenylfurfuran. The dibenzoylstilbenes used in the following experiments were prepared by Zinin's methods (Beilstein's *Handbuch*, 3rd ed., **3**, 311 and 312).

Three grams of dibenzoylstilbene (m. p. 220°) and 1·2 grams of a 50 per cent. solution of hydrazine hydrate were dissolved in absolute alcohol and boiled for $1\frac{1}{2}$ hours. On cooling, the solution deposited yellow needles which, by repeated recrystallisation from boiling alcohol, were obtained with the constant melting point of 207—208°. The yellow colour was not removed by boiling the solution with animal charcoal. The compound is difficult to burn and the figures for carbon are somewhat low.

0·1752 gave 0·5544 CO_2 and 0·0934 H_2O. C = 86·30; H = 5·94.
0·1774 „ 0·5594 CO_2 „ 0·0942 H_2O. C = 85·99; H = 5·90.
0·1763 „ 0·5570 CO_2 „ 0·0934 H_2O. C = 86·16; H = 5·89.
0·1722 „ 10·65 c.c. moist nitrogen at 11° and 757 mm. N = 7·34.
$C_{28}H_{22}N_2$ requires C = 87·05; H = 5·70; N = 7·25 per cent.

This is the formula of a tetraphenyldihydrodiazine. The formula of a tetraphenyldiazine, $C_{28}H_{20}N_2$, on the other hand, would require C = 87·50; H = 5·21; N = 7·29 per cent., and for this the value found for hydrogen is much too high. A portion of the hydrazine has therefore exercised a reducing action as in the case already described.

The compound is a 3 : 4 : 5 : 6-*tetraphenyldihydro*-1 : 2-*diazine*,

```
             N
           //  \
  C6H5·C        N
       |   H2   ||
  C6H5·C        C·C6H5 ,
          \\  /
            C
            ·
           C6H5
```

in which the position of the two additive hydrogen atoms has not yet been determined.

Dibenzoylstilbene (m. p. 232°)—"octahedral oxylepiden"—was then boiled with excess of hydrazine hydrate in alcoholic solution for 9 hours, renewing the hydrazine hydrate. On allowing the solution to cool, practically the whole of the dibenzoylstilbene (m. p. 232°) crystallised out unchanged. No new product could be detected.

The dibenzoylstilbene melting at 220° is therefore the *cis*-form; that melting at 232° the *trans*-form.

Action of Hydrazine on α-*Benzoyl*-β-*trimethacetylstyrene*,

```
C6H5·C==CH
     |   |
C6H5·CO CO·C(CH3)3
```

(m. p. 115°).—α-Benzoyl-β-trimethacetylstyrene was obtained by Japp and Maitland (Trans., 1904, **85**, 1496) by the condensation of benzil with methyl *tert*.-butyl ketone under the influence of alcoholic potassium hydroxide.

A mixture of benzoyltrimethacetylstyrene with an excess of hydrazine hydrate was dissolved in alcohol and boiled for 15 minutes. On cooling, the solution deposited wedge-shaped crystals, which, after recrystallisation from alcohol, melted constantly at 185—186°. The yield was good.

0·1738 gave 0·5288 CO_2 and 0·1094 H_2O. C = 82·98; H = 6·99.
0·1554 „ 12·97 c.c. moist nitrogen at 11° and 731 mm. N = 9·57.
$C_{20}H_{20}N_2$ requires C = 83·33; H = 6·95; N = 9·72 per cent.

The compound is 3 : 4-*diphenyl*-6-tert.-*butyl*-1 : 2-*diazine*,

```
               N
              //\
 (CH3)3C·C      N
         |      ||
        HC      C·C6H5 ·
          \\   /
            C
            |
           C6H5
```

Neither in the foregoing experiment, nor in one in which boiling acetic acid was used as a solvent for the interacting substances, could any trace of the corresponding dihydrodiazine be detected. The experiment in which acetic acid was employed yielded a very resinous product.

The α-benzoyl-β-trimethacetylstyrene melting at 115° is the only known form of this substance; but, as already mentioned, the ease with which it interacts with hydrazine to form a diazine leads us to assign to it the *cis*-configuration.

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LXXI.—*Condensations of Phenanthraquinone with Ketonic Compounds.*

By FRANCIS ROBERT JAPP, F.R.S., and JAMES WOOD, M.A., B.Sc., Carnegie Scholar in the University of Aberdeen.

VERY few condensations of phenanthraquinone with ketonic compounds have hitherto been studied, and in these only alkaline condensing agents have been employed; but in many cases such agents give no result.

We find, however, that acetic anhydride containing a little concentrated sulphuric acid frequently brings about the desired condensation. The reaction is occasionally complicated by the fact that in some cases the condensation product interacts further with the acetic anhydride.

3-*Acetoxy*-2-*phenyl*-4 : 5-*diphenylenefurfuran*,

```
C6H4·C——C·O·C2H3O
 |    ||  ||
C6H4·C   C·C6H5
      \  /
       O
```

(m. p. 232°).—Twenty grams of finely-powdered phenanthraquinone (free from anthraquinone*), 14 grams of acetophenone, 130 c.c. of

* The phenanthraquinone used for these reactions must be purified by means of the hydrogen sodium sulphite compound, as some of the products are almost impossible to separate from the anthraquinone which will otherwise contaminate them.

acetic anhydride, and 50 drops of concentrated sulphuric acid, were introduced into a flask fitted with a short open tube, and the flask was immersed in water kept at a temperature of 40—50°, whilst the mixture was shaken from time to time. In the course of 30—40 hours the whole of the phenanthraquinone had disappeared, and the liquid was filled with long, slender, almost colourless needles; these were separated by filtration and purified by recrystallisation from boiling benzene, decolorising with animal charcoal if necessary. The substance was thus obtained in slender needles, melting at 232°. The yield was 20 grams.

0·1386 gave 0·4139 CO_2 and 0·0576 H_2O. C = 81·44; H = 4·62.
0·1757 „ 0·5246 CO_2 „ 0·0744 H_2O. C = 81·43; H = 4·71.
$C_{24}H_{16}O_3$ requires C = 81·82; H = 4·55 per cent.

The formation of this compound may be explained on the assumption that the unknown phenanthroxyleneacetophenone,

$$\begin{array}{l} C_6H_4\cdot C{=}CH \\ C_6H_4\cdot CO\ \ CO\cdot C_6H_5 \end{array},$$

is first formed; this compound then unites with acetic acid, and the additive compound parts with water:

$$\begin{array}{l} C_6H_4\cdot C{=}CH \\ C_6H_4\cdot CO\ \ CO\cdot C_6H_5 \end{array} \xrightarrow{C_2H_4O_2} \begin{array}{l} C_6H_4\cdot CH\cdot CH\cdot O\cdot C_2H_3O \\ C_6H_4\cdot CO\ \ CO\cdot C_6H_5 \end{array}$$

$$\xrightarrow{-H_2O} \begin{array}{l} C_6H_4\cdot C{-}C\cdot O\cdot C_2H_3O \\ C_6H_4\cdot C\ \ \ C\cdot C_6H_5 \\ \quad\quad\quad O \end{array}.$$

The compound would thus be *3-acetoxy-2-phenyl-4:5-diphenylenefurfuran*, and the transformation of the hypothetical intermediate product, phenanthroxyleneacetophenone, is strictly analogous to that which dibenzoylstyrene, $\begin{array}{l} C_6H_5\cdot C{=}CH \\ C_6H_5\cdot CO\ \ CO\cdot C_6H_5 \end{array}$, undergoes when it is converted, by the action of acetic anhydride containing a little sulphuric acid, into 3-acetoxy-2:4:5-triphenylfurfuran, $\begin{array}{l} C_6H_5\cdot C{-}C\cdot O\cdot C_2H_3O \\ C_6H_5\cdot C\ \ \ C\cdot C_6H_5 \\ \quad\quad\quad O \end{array}$

(J. Thiele, *Ber.*, 1898, 31, 1248).

Ethyl Diphenylenedibenzoylmuconate (*Ethyl βγ-diphenylene-αδ-dibenzoylbutadiene-αδ-dicarboxylate*), $\begin{array}{l} C_6H_4\cdot C{:}C(CO\cdot C_6H_5)\cdot CO_2\cdot C_2H_5 \\ C_6H_4\cdot C{:}C(CO\cdot C_6H_5)\cdot CO_2\cdot C_2H_5 \end{array}$.— Ten grams of finely powdered phenanthraquinone, 12 grams of ethyl benzoylacetate, and 40 c.c. of acetic anhydride containing 16 drops of

concentrated sulphuric acid were employed in this experiment, which was conducted like that already described. After heating continuously at 40—50° for nearly 100 hours, the whole of the phenanthraquinone had disappeared. The mixture was allowed to cool; the crystalline product was separated by filtration, washed with a little cold glacial acetic acid, and recrystallised from boiling benzene, in which it is fairly soluble. It was thus obtained in clear, rectangular plates with bevelled edges (yield: 10 grams). It softens and almost melts between 170° and 174°, but immediately resolidifies, finally melting sharply at 223°. This latter melting point, however, is that of an isomeride into which the original condensation compound is transformed by heating (*vide infra*).

0·1912 gave 0·5433 CO_2 and 0·0883 H_2O. C = 77·49; H = 5·13.
0·1705 „ 0·4838 CO_2 „ 0·0784 H_2O. C = 77·39; H = 5·11.
0·1832 „ 0·5200 CO_2 „ 0·0846 H_2O. C = 77·39; H = 5·13.
$C_{36}H_{28}O_6$ requires C = 77·70; H = 5·04 per cent.

The compound, which is *ethyl diphenylenedibenzoylmuconate* (*vide supra*), is formed from phenanthraquinone and ethyl benzoylacetate according to the equation:

$$\begin{array}{l} C_6H_4\cdot CO \\ | \qquad\ \ | \\ C_6H_4\cdot CO \end{array} + 2C_6H_5\cdot CO\cdot CH_2\cdot CO_2\cdot C_2H_5 = \begin{array}{l} C_6H_4\cdot C:C(CO\cdot C_6H_5)\cdot CO_2\cdot C_2H_5 \\ | \qquad\ \ | \\ C_6H_4\cdot C:C(CO\cdot C_6H_5)\cdot CO_2\cdot C_2H_5 \end{array} + 2H_2O,$$

the acetic anhydride in this case furnishing no part of the resultant molecule.

Attempts to hydrolyse this ester with alcoholic sodium hydroxide yielded no definite product. No acid could be obtained from the alkaline solution.

Isomeride (m. p. 223·5°) *of Ethyl Diphenylenedibenzoylmuconate.*— Five grams of ethyl diphenylenedibenzoylmuconate were heated in a test-tube by means of a glycerol bath until the substance, after softening and resolidifying between 170° and 174°, as above described, finally melted at 223°. No gas was given off during the process, and the tube with the product was found to weigh practically the same as before. The product was recrystallised from boiling glacial acetic acid, from which it was deposited in short yellowish needles, melting constantly at 223·5°. The yield is quantitative.

0·1635 gave 0·4646 CO_2 and 0·0756 H_2O. C = 77·49; H = 5·14.
$C_{36}H_{28}O_6$ requires C = 77·70; H = 5·04 per cent.

The compound is therefore isomeric with ethyl diphenylenedibenzoyl-

muconate. Provisionally it may be named *ethyl* iso*diphenylenedibenzoylmuconate.*

Hydrolysed with alcoholic sodium hydroxide it yields an acid, which, however, has not yet been obtained in quantity sufficient for examination.

The fact that ethyl diphenylenedibenzoylmuconate, unlike its isomeride, does not yield an acid under the foregoing conditions, points to a difference in constitution between the two compounds more fundamental than that of mere *cis* and *trans* isomerism—the explanation which would perhaps first suggest itself. Possibly the isomerisation under the influence of heat occurs according to the scheme:

$$\begin{array}{l} C_6H_4\cdot C{:}C(CO\cdot C_6H_5)\cdot CO_2\cdot C_2H_5 \\ C_6H_4\cdot C{:}C(CO\cdot C_6H_5)\cdot CO_2\cdot C_2H_5 \end{array} \longrightarrow \begin{array}{l} C_6H_4\cdot C\cdot C(CO\cdot C_6H_5)\cdot CO_2\cdot C_2H_5 \\ C_6H_4\cdot C\cdot C(CO\cdot C_6H_5)\cdot CO_2\cdot C_2H_5 \end{array},$$

in which case ethyl diphenylenedibenzoylmuconate would have somewhat the same relation to ethyl *iso*diphenylenedibenzoylmuconate that cinnamic acid has to β-truxillic acid, except that in the present case the polymerisation is intramolecular, not intermolecular.

We have also obtained condensation products of phenanthraquinone with ethyl acetoacetate and with ethyl malonate. We wish to reserve the study of the various condensations of this class.

We have to thank the Council of the Royal Society for an allotment from the Government Grant in aid of the work described in this and the preceding paper.

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LXXII.—*Cyanomaclurin.*

By ARTHUR GEORGE PERKIN, F.R.S.

SOME years ago (Trans., 1895, **67**, 939) it was shown that the Indian dyestuff Jackwood (*Artocarpus integrifolia*) contains, in addition to morin, a new substance, to which the name cyanomaclurin was assigned. This compound crystallised in colourless prisms, gave numbers in fair agreement with the formula $C_{15}H_{12}O_6$ or $C_{18}H_{16}O_7$, and possessed the characteristic property that its alkaline solution on warming developed a deep indigo-blue coloration. A disazobenzene derivative was prepared, but other crystalline derivatives could not at the time be produced according to the ordinary methods. Owing to a lack of the raw

material it was not possible to make a more complete examination of this compound, but it was then noticed that in certain important respects its properties were similar to those of catechin, the colourless crystalline constituent of gambier catechu. During a recent investigation of the latter compound (Trans., 1902, **81**, 1160) this resemblance again came to mind, and strikingly so, because the molecular weight of catechin was then found to be represented as $C_{15}H_{14}O_6$ and not $C_{21}H_{20}O_9$, as was proposed by earlier workers. Again, the analytical results given by these substances were nearly identical. It therefore appeared possible that cyanomaclurin and the catechins were not only isomeric but members of the same group, and the present work was undertaken with the hope of elucidating this point. The isolation of cyanomaclurin from the wood is extremely tedious and the yield of pure substance is small, so that for the purpose of this investigation about 150 lbs. of the raw material have been found necessary. Through the kindness of Messrs. Wood and Bedford, of Leeds, this amount was readily procured.

Experimental.

The cyanomaclurin was prepared by the method previously employed but the details of purification were somewhat different. The crude product obtained by the evaporation of the ethyl acetate extract was freed as thoroughly as possible from adhering viscous matter, ground up with a trace of acetate, collected and dried. The finely-ground substance, in quantities of about 15 grams, was stirred into 50 c.c. of warm water, collected at the pump, and treated in a similar manner until the filtrate was almost colourless. There were thus obtained 6·25 grams of a nearly colourless, crystalline powder, which, although not quite pure, could be employed for most purposes. In special cases, the substance was crystallised from water, an extremely tedious method, for crystals do not usually separate until the solution has stood for several days, and even then the separation is very slow and the yield extremely poor; again, crystallisation from ethyl acetate was sometimes employed. On concentrating the aqueous mother liquors, a second deposit does not separate, but the dissolved substance may be recovered by saturating the solution with salt and agitation with ethyl acetate. Pure cyanomaclurin dried at the ordinary temperature is anhydrous, and does not suffer loss even at 160°. It does not appear to possess a definite melting point, but on heating to a high temperature slowly decomposes; thus at 290° it became extremely dark, but had not fused.

As is well known, solutions of catechin from gambier catechu and acacatechin from acacia catechu give with pine wood and hydrochloric

acid the phloroglucinol reaction, and it was now found that cyanomaclurin behaved in an identical manner. This was interesting, for although, as previously pointed out, maclurin, phloretin, and hesperitin (*loc. cit.*) give an analogous coloration, the reaction with the catechins and cyanomaclurin is much more rapid, in fact, as much so as with phloroglucinol itself.

Fusion with Alkali.—As cyanomaclurin was not previously suspected to contain a phloroglucinol nucleus, this decomposition was again studied. The substance was heated with caustic potash and a little water to 200—220° for half an hour, the melt dissolved in water and neutralised with acid. Ether extracted from this solution a crystalline substance which was dissolved in water and the liquid saturated with sodium hydrogen carbonate. Ether now removed from the mixture a product which, after washing with hot benzene and crystallisation from water, formed colourless needles, which melted at 210° and had all the properties of phloroglucinol.

Found C = 57·05; H = 4·77. $C_6H_6O_3$ requires C = 57·14; H = 4·76 per cent.

The sodium hydrogen carbonate solution was neutralised with acid, and from this ether now extracted a colourless acid which was purified by crystallisation from water.

Found C = 54·24; H = 4·11. $C_7H_6O_4$ requires C = 54·54; H = 3·89 per cent.

It formed colourless needles melting at 206°, and was found to consist of *β-resorcylic acid.* In the previous communication, it was suggested that this acid was a methylresorcylic acid (cresorcylic acid) and indeed these two substances are very similar in general properties, but as analysis now shows this cannot be the case.

The benzene extracts obtained during the purification of the phloroglucinol were evaporated to a small bulk, and on standing deposited crystals. These melted at 104° and consisted of *resorcinol*, derived no doubt from the action of the alkali on the β-resorcylic acid.

An interesting resemblance is therefore to be observed between morin and cyanomaclurin, which exist side by side in this dye-wood, for on hydrolysis both yield phloroglucinol and β-resorcylic acid. Curiously enough, it has been previously pointed out that the constituents of gambier and acacia catechus possess a similar relationship, in that quercetin, catechin, and acacatechin on fusion with alkali give in each case phloroglucinol, and protocatechuic acid.

Disazobenzene cyanomaclurin, previously described, was again prepared and re-examined. Five grams of cyanomaclurin yielded 8·5 grams, or 170 per cent. of this compound, and this result is comparable

with that of gambier catechin, which in like manner gave 170 per cent. of disazobenzene catechin.

Found C = 64·94 ; H = 4·36 ; N = 11·48 per cent.
$C_{15}H_{10}O_6(C_6H_5N_2)_2$ requires C = 65·32 ; H = 4·03 ; N = 11·29 per cent.
$C_{15}H_{12}O_6(C_6H_5N_2)_2$ requires C = 65·06 ; H = 4·41 ; N = 11·24 per cent.

In the earlier communication, the percentages C = 65·11, H = 4·46, N = 10·92 were obtained.

This substance is therefore very similar in composition to the corresponding catechin compounds, and these it closely resembles in general properties, with the exception that it is somewhat more soluble in hot alcohol. In the crude condition, it readily dissolves in this solvent, but on heating the liquid crystallisation soon commences, and these crystals now require a considerable quantity of alcohol for re-solution. When heated, disazobenzene cyanomaclurin sinters at about 225°, and melts at 245—247° with decomposition.

The acetyl derivative is readily prepared by boiling with acetic anhydride for three hours. On diluting the hot solution cautiously with alcohol, crystals separated which were collected, redigested for a short time with acetic anhydride, and finally crystallised from benzene with the aid of animal charcoal.

Found C = 63·61 ; H = 4·46 ; N = 9·43, 9·49.
$C_{15}H_7O_6(C_6H_5N_2)_2(C_2H_3O)_3$ requires C = 63·66 ; H = 4·18 ; N = 9·00 per cent.
$C_{15}H_9O_6(C_6H_5N_2)_2(C_2H_3O)_3$ requires C = 63·46 ; H = 4·48 ; N = 8·97 per cent.

This compound, probably a triacetyl derivative, forms orange-red needles melting at 209—210°, and resembles in general properties the corresponding acetyl disazobenzene catechins.

Acetylcyanomaclurin could not be prepared in the crystalline condition by the ordinary methods, but the pyridine process eventually gave a better result. Two grams of cyanomaclurin were dissolved in 30 grams of pyridine, the solution placed in a freezing mixture, and 8·5 grams of acetyl chloride added drop by drop, well shaking after each addition. After standing for ten minutes, the product was poured on to ice, the colourless precipitate was collected and drained on tile, and then dissolved in a mixture of hot acetone and alcohol, from which, on cooling, a viscous mass separated. Other preparations behaved similarly, but eventually one of these, on standing for several weeks, became crystalline, and by the aid of these crystals other products were readily obtained in the same condition. By repeated crystallisation from a mixture of acetone and alcohol, employing animal charcoal, it formed colourless needles melting at 136—138°.

Found C = 59·91 ; H = 4·74.

$C_{15}H_9O_6(C_2H_3O)_5$ requires C = 60·00 ; H = 4·80 per cent.

$C_{15}H_7O_6(C_2H_3O)_5$ „ C = 60·24 ; H = 4·41 „

A molecular weight determination by the cryoscopic method gave the following result:

0·5138 in 13·71 naphthalene gave Δt = 0·515. M. W. = 509.

$C_{25}H_{22}O_{11}$ requires M. W. = 498.

Benzoylcyanomaclurin was prepared by the pyridine method and is crystallised more readily than the acetyl derivative. For this purpose, 1 gram of cyanomaclurin, 15 grams of pyridine, and 11·5 grams of benzoyl chloride were employed, and after twelve hours the product was poured into water and the viscous residue dissolved in its own bulk of alcohol. Crystals gradually separated which were recrystallised twice from a mixture of acetone and alcohol.

Found C = 74·01 ; H = 4·11.

$C_{15}H_7O_6(C_7H_5O)_5$ requires C = 74·25 ; H = 3·96 per cent.

$C_{15}H_9O_6(C_7H_5O)_5$ „ C = 74·07 ; H = 4·19 „

It crystallised in colourless prisms, melting at 171—173°; it was sparingly soluble in cold alcohol, and very similar in appearance to pentabenzoylacacatechin (*loc. cit*). Molecular weight determinations gave the following results:

0·509 in 13·47 naphthalene gave Δt = 0·315. M. W. = 839.

0·5396 in 13·51 naphthalene „ Δt = 0·345. M. W. = 811.

$C_{50}H_{32}O_{11}$ requires M. W. = 808.

These results therefore indicate that cyanomaclurin has the formula $C_{15}H_{14}O_6$ or $C_{15}H_{12}O_6$, and the former appeared most likely owing to the resemblance of its general properties with those of the catechins. Analyses of specimens purified by distinct methods gave percentages of hydrogen which, however, taken as a whole, are in better agreement with $C_{15}H_{12}O_6$, and this must without doubt represent the true formula for this substance.

Found C = 62·46, 62·65, 62·28, 62·32, 62·13 ; H = 4·25, 4·35, 3·96, 4·36, 4·15.

$C_{15}H_{12}O_6$ requires C = 62·50 ; H = 4·16 per cent.

$C_{15}H_{14}O_6$ „ C = 62·07 ; H = 4·82 „

Numerous attempts to prepare a crystalline methyl ether of cyanomaclurin were unsuccessful, either with methyl iodide or methyl sulphate. The product thus obtained consisted of a colourless, viscous mass, and this on acetylation by the pyridine method did not yield a well-defined substance. It was, however, very interesting to observe that

if this methylated cyanomaclurin was dissolved in acetic acid and the solution treated with a few drops of nitric acid a bluish-green liquid was formed which rapidly assumed a pure blue tint. This reaction is identical with that given under similar conditions by the catechin tetramethyl ethers (Trans., 1905, **87**, 400).

It was previously pointed out that when an aqueous solution of cyanomaclurin is treated with mineral acids reddish-brown, amorphous substances are formed, which vary in solubility according to the duration of the action and resemble the so-called catechin anhydrides described by Etti (*Annalen*, 1887, **186**, 327) and Kraut and Delden (*Annalen*, 1877, **186**, 332). It was also suggested that the alteration of the freshly cut wood from a yellow to a mahogany tint on long keeping was the result of the production of one or other of these substances. The most definite of these reddish-brown substances is the final compound thus obtained, and this was examined because it was unlikely to be a mixture and could be compared with the corresponding anhydrides of catechin and acacatechin.

One gram of cyanomaclurin dissolved in 100 c.c. of acetic acid was treated with 10 c.c. of hydrochloric acid and the solution digested at the boiling heat. The deep brown liquid rapidly deposited an amorphous precipitate, and this was collected hot, washed several times with acetic acid, and finally with alcohol. The yield was 0·79 gram.

Found at 160°: C = 63·11, 63·48, 63·53; H = 3·75, 3·94, 3·99 per cent.

The product consisted of a reddish-brown powder, insoluble in alkaline solutions and apparently in all solvents. Prepared as above, it obstinately retains alcohol or water even at 100°, and is only obtained in the anhydrous condition by prolonged heating at 160°. It is also readily produced if the hydrochloric acid is replaced by a small quantity of sulphuric acid. The molecular weight of this substance is most probably extremely high, and no attempt has been made to deduce a formula from the above percentages; it is, however, interesting to note that these figures are practically identical with those given by the corresponding derivatives of catechin (C = 63·26; H = 3·89) and acacatechin (C = 63·33; H = 3·94), and this again points to the close relationship between these substances. As is well known, this so-called anhydride or phlobophane production by means of mineral acids is characteristic of numerous tannins of the catechol class, and is presumed to be an indication of the presence of such a substance. The behaviour of cyanomaclurin in this respect indicates that the presence of a catechol nucleus is not essential for phlobophane formation, and this has been previously suggested because a novel tannin compound existing in the leaves of the *Pistachia lentiscus*

(Trans., 1898, **73**, 378), and in which only pyrogallol and phloroglucinol nuclei are present, also gave a similar product. Evidently therefore this reaction is due rather to the structure of the compounds in question than to the presence of one special phenolic nucleus.

Experiments on the oxidation of an aqueous solution of cyanomaclurin with potassium ferricyanide in the presence of sodium acetate gave negative results, and no colouring matter analogous to that produced in this manner from the catechins could be obtained.

Summary of Results.

The results of this investigation indicate an extremely close relationship between cyanomaclurin and the catechins, and it at one time appeared probable that the former differed merely from one or other of the latter in that it contained a resorcinol instead of a catechol nucleus. The number of hydroxyls and the general reactions of these substances are almost identical in each case, except in so far as the colour reactions due to distinct nuclei would lead one to expect a slight difference; but, on the other hand, as the formula of cyanomaclurin is $C_{15}H_{12}O_6$, it cannot be isomeric with the catechins but must belong to a distinct group. It is interesting to note how clearly the two nuclei phloroglucinol and catechol and phloroglucinol and resorcinol respectively are to be observed in catechin and cyanomaclurin, the first-named by the method previously referred to, and the second by means of ferric chloride. Thus catechin in this way gives the green catechol coloration, and cyanomaclurin a liquid very similar to that yielded by resorcinol itself.

Quercetin and catechin exist side by side in catechu, and it was previously suggested that the latter could be regarded as a reduction product of the former; again, a similar reasoning would apply to morin and cyanomaclurin, for these are found together in the Jackwood, and yield on hydrolysis identical products. It is therefore considered probable that the following constitution is applicable to cyanomaclurin:

```
            O        OH
   OH/\  /\C-----<    >OH,
     |  |  ||
     \/\/ C·OH
    OH  CH2
```

for although it could be represented as a hydroxychalkone, thus:

```
                              OH
  OH/\OH
    |  |-CO·CH:CH-<    >OH,
     \/
     OH
```

it does not possess the characteristics of this class of compound. As an alternative formula, the following is also possible :

O
OH CH
C·OH OH
OH CH——— OH.

The rarity of cyanomaclurin and the difficulty with which it yields crystalline derivatives render it probable that these points will only be definitely solved by the synthetical preparation of the substance itself.

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CLOTHWORKERS' RESEARCH LABORATORY,
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LEEDS.

LXXIII.—*Studies in the Camphane Series. Part XIX. Camphoryl-ψ-semicarbazide.*

By MARTIN ONSLOW FORSTER and HANS EDUARD FIERZ.

THE main distinction between Rupe's camphorylcarbamide and the *pseudo*-modification recently described by us (this vol., p. 110), lies in their behaviour towards nitrous acid, which transforms the first-named into camphorylcarbimide, whilst yielding a nitroso derivative with the isomeride. If the freshly prepared nitroso-compound is suspended in dilute acetic acid and treated with zinc dust, it quickly forms a clear solution, from which we have isolated a crystalline compound,

$$C_{11}H_{19}O_2N_3,$$

melting at 193°, and having the properties of a primary semicarbazide.

In view of the probable relationship between camphorylcarbamide and its *pseudo*-modification, developed in the paper quoted, we regard the new substance as *camphoryl-ψ-semicarbazide*,

$$C_8H_{14}<\begin{matrix}CH\cdot N(NH_2)\\ | \\ C(OH)-NH\end{matrix}>CO,$$

and as it appears to be the first optically active primary semicarbazide, we have examined it in some detail.

Naturally the chief point of interest in connection with such a substance is its behaviour towards aldehydes and ketones, because an agent by which racemic compounds of those classes may be resolved into their active compounds might find useful application; phenyl-*d*-amylhydrazine, $C_2H_5\cdot CH(CH_3)\cdot CH_2\cdot N(C_6H_5)\cdot NH_2$, quite recently described by Neuberg and Federer (*Ber.*, 1905, **38**, 866), seems to achieve satisfactorily the purpose in question, but its production involves the troublesome isolation of an optically active amyl halide.

Camphoryl-ψ-semicarbazide condenses easily with most aldehydes and some ketones, the readiness with which action takes place among the substituted benzaldehydes being extraordinary; on treating a 0·5 per cent. solution of the base in water with the calculated amount of benzaldehyde, the liquid requires to be warmed no longer than one minute before it becomes turbid, the crystalline semicarbazone separating almost immediately afterwards. The condensation products which have been obtained in this manner from a number of typical aldehydes are characterised in many cases by unusually high specific rotatory power; the *pseudo*-semicarbazide itself has $[\alpha]_D$ 8·6°, but the benzylidene compound has $[\alpha]_D$ 420·6°, and the cinnamylidene derivative $[\alpha]_D$ 605·4°, whilst the product from benzoquinone has $[\alpha]_D$ −1051° in acetone. This is not the highest specific rotatory power on record, because parasantoninimide, described by Francesconi (*Atti R. Accad. Lincei*, 1903, [v], **12**, ii, 204), has $[\alpha]_D$ +1135°; this corresponds to $[M]_D$ 2780°, however, whereas benzoquinone camphoryl-ψ-semicarbazone has $[M]_D$ 3310°. In the following table, the values for the vanillidene, cuminylidene, and *o*-hydroxybenzylidene compounds are only approximate, owing to the retention of crystal solvent by these derivatives, allowance being therefore made in the calculation.

ψ-Semicarbazone.	M. p.	Solvent.	$[\alpha]_D$.	$[M]_D$.
m-Nitrobenzaldehyde	218°	Acetic acid	+84°	301°
Acetone	217	Chloroform	−188	498
o-Hydroxybenzaldehyde.	212	,,	+283	931
Camphorquinone	234	,,	−314	1172
Vanillin	219	,,	+376	1349
Cuminaldehyde............	229	,,	+415	1473
Benzaldehyde..............	223	,,	+421	1318
Anisaldehyde.........	234	,,	+440	1509
Piperonaldehyde	229	,,	+450	1599
Furfuraldehyde	222	,,	+502	1522
Cinnamaldehyde	219	Ether	+605	2051
p-Benzoquinone............	197	Acetone	−1051	3310

Several points of interest are presented by this list, and will receive more extended study. The high rotation of the benzylidene compound, which has $[\alpha]_D$ almost identical with that of benzylidene-camphor, suggested an examination of the cinnamaldehyde derivative, many investigators having shown that double linkages exert a profound influence on specific rotatory power. From this we were led to the product from *p*-benzoquinone, because in that substance the ordinary benzenoid structure is suspended, and no fewer than four double linkages may be recognised.

An illustration of the marked effect on specific rotatory power brought about by unsaturated linkages in this series may be drawn from the various compounds arising by replacement of iminic hydrogen in camphoryl-ψ-carbamide, $C_8H_{14}<\begin{matrix}CH\text{——}NH\\ C(OH)\cdot NH\end{matrix}>CO$, which is represented in the following table by the symbol Cam.NH :

ψ-Carbamide	Cam.NH	$[\alpha]_D$	−13·5°
Methyl ψ-carbamide	Cam.N·CH_3		+6·9
Nitroso-ψ-carbamide	Cam.N·N:O		+169·3
ψ-Semicarbazide	Cam.N·NH_2		+8·9
Benzaldehyde ψ-semicarbazone	Cam.N·N:CH·C_6H_5		+421
Cinnamaldehyde ψ-semicarbazone	Cam.N·N:CH·CH:CH·C_6H_5		+605
Benzoquinone ψ-semicarbazone	Cam.N·N:C$<\begin{matrix}CH:CH\\ CH:CH\end{matrix}>$C:O.		−1051

Although perhaps merely a coincidence, it is remarkable that the algebraic difference in rotatory power between the *pseudo*-carbamide and the nitroso-derivative should be 182·8°, and therefore almost identical with that shown by the *pseudo*-semicarbazones of benzaldehyde and cinnamaldehyde, namely, 184°, the principal difference between the individuals of each pair being a single ethylenic linkage.

It is also noteworthy that the specific rotation of the *pseudo*-semicarbazones of acetone and the two quinones should be negative, whilst the condensation products from the aldehydes are dextrorotatory. Moreover, it will be observed that if the above formula correctly represents the constitution of the *pseudo*-carbamide, it contains two asymmetric carbon atoms in addition to those present in camphor itself ; consequently, the *pseudo*-carbamide and the *pseudo*-semicarbazide, although optically active, are racemic with respect to those carbon atoms, and it may be possible, by fractionally crystallising the camphoryl-ψ-semicarbazone of an optically active ketone such as camphor, to resolve the *pseudo*-semicarbazide itself into enantiomorphous modifications. One of these new forms should yield with benzoquinone a *pseudo*-semicarbazone having $[\alpha]_D$ in excess of that recorded for the racemoid.

The members of the camphoryl-ψ-semicarbazone group are character-

ised by the tenacity with which they retain solvents of crystallisation, particularly in the cases of alcohol and benzene; the same feature was noticed in connection with the isomeric camphorylcarbamides (this vol., p. 115), but the high specific rotation of the *pseudo*-semicarbazones renders it possible to emphasise this point by polarimetric observations. The following values have been observed for the cinnamylidene derivative, and illustrate forcibly the words recently used by Walden (*Ber.*, 1905, 38, 402), "es giebt keine indifferenten Lösungsmittel."

Solvent.	$[\alpha]_D$.	Solvent.	$[\alpha]_D$.
Ether	+605°	Nitromethane	+307°
Chloroform...............	527	Acetone..................	162
Phenetole	451	Alcohol..................	107
Bromobenzene	438	Acetic acid	96
Carbon disulphide......	331	Pyridine	−54

Similarly, the benzoquinone compound, which gives $[\alpha]_D$ −1051° in acetone, has $[\alpha]_D$ −545° in alcohol, whilst the furfural derivative gives $[\alpha]_D$ 502° and $[\alpha]_D$ 100·5° in chloroform and alcohol respectively.

Before proceeding to the experimental section, attention should be drawn to the readiness with which camphoryl-ψ-semicarbazide furnishes a monomolecular anhydride, produced by the action of hydrochloric acid. The constitution of this compound might be represented by the formulæ

$$C_8H_{14}\left<\begin{matrix} CH-N \\ | \quad NH \\ C-NH \end{matrix}\right>CO \quad \text{and} \quad C_8H_{14}\left<\begin{matrix} CH\cdot N(NH_2) \\ | \\ C=\!=\!=N \end{matrix}\right>CO,$$

of which the second is that of camphoraminoimidazolone. This would exhibit properties recalling those of the *pseudo*-semicarbazide, and, as the anhydride obtained in the manner described has no action on ammoniacal silver oxide and does not undergo condensation with aldehydes, we believe it to have the structure represented by the first of the above formulæ.

The behaviour of camphoryl-ψ-semicarbazide towards Fehling's solution is remarkable; hot alkalis have no action on the substance, but the agent mentioned oxidises it to camphor immediately on warming the liquid, and simultaneously eliminates nitrogen and cyanic acid,

$$C_8H_{14}\left<\begin{matrix} CH-\!-\!-N\cdot NH_2 + O \\ | \qquad\quad CO \\ C(OH)-\!-NH \end{matrix}\right. = C_8H_{14}<\begin{matrix}CH_2\\ | \\ CO\end{matrix} + N_2 + H_2O + HNCO,$$

the presence of which in the liquid has been definitely established. Mercury acetamide also liberates nitrogen from the *pseudo*-semicarbazide (compare Trans., 1898, **73**, 783) without giving rise to camphor.

EXPERIMENTAL.

Camphoryl-ψ-semicarbazide, $C_8H_{14}<\begin{matrix}CH\cdot N(NH_2)\\ | \\ C(OH)-NH\end{matrix}>CO$.

By a slight modification of the process described (this vol., p. 110), camphoryl-ψ-carbamide may be obtained in a condition which renders unnecessary the crystallisation from boiling water as a step preparatory to conversion into the nitroso-derivative; this consists in extracting twice with ether the solution of aminocamphor hydrochloride before treatment with potassium cyanate. Thus, the production of the *pseudo*-semicarbazide from *iso*nitrosocamphor may be carried out rapidly and economically.

Thirty-five grams of camphoryl-ψ-carbamide were transformed into the nitroso-derivative (*loc. cit.*), and the undried product, suspended in 600 c.c. of water with 60 c.c. of glacial acetic acid, was treated with 25 grams of zinc dust, the temperature being kept low by a liberal supply of crushed ice. The nitroso-derivative rapidly disappeared, and, when action was complete, the colourless liquid was filtered from undissolved zinc and concentrated on the water-bath until about 150 c.c. remained; on adding 75 c.c. of ammonia (sp. gr. 0·88), which is sufficient to redissolve the zinc hydroxide, a crystalline precipitate of the *pseudo*-semicarbazide was formed, a further quantity being obtained from the filtrate by adding acetone, the *pseudo*-semicarbazone of which is precipitated a few seconds afterwards. The *pseudo*-semicarbazide still retained some zinc hydroxide, and was therefore crystallised from a small quantity of boiling water containing ammonia, being afterwards dried in the desiccator and recrystallised from chloroform, which deposited snow-white needles melting at 193°.

0·1488 gave 0·3194 CO_2 and 0·1139 H_2O. C = 58·54; H = 8·50.
0·1234 ,, 20·4 c.c. nitrogen at 19° and 752 mm. N = 18·80.
$C_{11}H_{19}O_2N_3$ requires C = 58·66; H = 8·44; N = 18·66 per cent.

A solution containing 0·8463 gram in 25 c.c. of water to which a few drops of alcohol had been added gave α_D 0°35′ in a 2-dcm. tube, whence $[\alpha]_D$ 8·6°.

The *pseudo*-semicarbazide is insoluble in petroleum and sparingly soluble in benzene, from which it separates in crystals retaining the solvent; it is moderately soluble in warm chloroform and cold water, but dissolves very freely in cold alcohol. In the purified condition, it is a stable substance, but freshly precipitated moist specimens slowly

undergo oxidation when exposed to air, developing the odour of camphor; it reduces cold ammoniacal silver oxide, from which a mirror is deposited on warming. Ferric chloride liberates nitrogen from an aqueous solution, giving rise to a white precipitate, and platinum tetrachloride forms a dark brown liquid from which nitrogen is slowly evolved. Fehling's solution has no action until heated, when brisk disengagement of nitrogen occurs, cuprous oxide being precipitated; camphor distils in the escaping steam, and if the experiment is conducted with a few decigrams of material, it can be shown by means of the cobalt test that potassium cyanate is present in the residual liquid. The substance itself is not volatile in steam, and is not removed from aqueous solutions by ether; alkalis are without action upon it, but hot hydrochloric acid transforms it into the anhydride (see page 734).

The *nitrate* is prepared most conveniently from the acetone-ψ-semicarbazone; this is dissolved in nitric acid (sp. gr. 1·42), forming a pale yellow syrup smelling strongly of acetone, and, on adding 10 volumes of pure ether, a clear solution is produced, setting almost immediately to a transparent jelly, which changes in the course of a few minutes to a compact mass of small, silky needles.

0·1496 gave 25·8 c.c. nitrogen at 20° and 758 mm. N = 19·68.

$C_{11}H_{19}O_2N_3,HNO_3$ requires N = 19·44 per cent.

The salt is insoluble in ether, but dissolves very freely in water, forming a solution which is strongly acid to litmus.

The *cuprinitrate* separates in the form of a pale blue, crystalline precipitate when a concentrated solution of copper nitrate in alcohol is added to the *pseudo*-semicarbazide nitrate dissolved in water; recrystallisation from hot absolute alcohol yields aggregates of lustrous, flat, bright blue needles. Two separately prepared specimens were analysed.

0·1505 gave 0·0154 CuO. Cu = 8·17.

0·0749 „ 0·0077 CuO. Cu = 8·21.

$(C_{11}H_{19}O_2N_3,HNO_3)_2,Cu(NO_3)_2$ requires Cu = 8·31 per cent.

The salt decomposes at 168—170°.

The Camphoryl-ψ-semicarbazones.

In preparing the condensation derivatives of camphoryl-ψ-semicarbazide with aldehydes and ketones, it has been the practice to employ the solution in dilute acetic acid obtained on filtering undissolved zinc from the reduced nitroso-derivative of the *pseudo*-carbamide. On adding rather less than the calculated amount of the aldehyde or

ketone to this liquid and raising the temperature to 80°, the carbonyl compound usually dissolved, separating almost immediately afterwards as the *pseudo*-semicarbazone, which was often sticky at first, but soon became crystalline.

Many of the condensation products thus obtained have been found to retain with great tenacity the solvents from which they crystallise. The cinnamylidene compound, for example, dissolves in a small proportion of cold benzene, but separates immediately in crystals containing one molecular proportion of the hydrocarbon, and in this form dissolves with difficulty in boiling benzene; so closely is the solvent attached to this compound that the crystals may be dissolved in chloroform and recovered from this medium by evaporation without displacement of benzene occurring. The vanillidene derivative behaves in the same way, but the analytical results in this case were less definite, falling short of those required by one molecular proportion of benzene. The cuminylidene compound, when crystallised from alcohol, also contains the solvent, whilst the condensation product from salicylaldehyde, doubtless owing to the presence of a hydroxyl group, furnished results agreeing with water of crystallisation. The substances obtained from benzaldehyde, *m*-nitrobenzaldehyde, anisaldehyde, piperonaldehyde, acetone, furfuraldehyde, camphorquinone, and *p*-benzoquinone, were solvent-free, but in several of these cases an alteration in the appearance of crystals freshly withdrawn from the mother-liquor indicates a tendency to combine with the solvent.

Benzaldehyde camphoryl-ψ-semicarbazone,

$$C_8H_{14}<\begin{matrix}CH\cdot N(N:CH\cdot C_6H_5) \\ | \\ C(OH)\text{———————}NH\end{matrix}>CO,$$

is readily soluble in cold chloroform, alcohol, ethyl acetate, and glacial acetic acid, dissolving to a moderate extent in boiling acetone, from which it separates in well-formed, six-sided prisms; it is almost insoluble in boiling light petroleum and cold ether, and melts at 223°, when it decomposes.

0·1806 gave 0·4566 CO_2 and 0·1242 H_2O. C = 68·95; H = 7·64.
0·1606 ,, 19·0 c.c. of nitrogen at 18° and 753 mm. N = 13·54.
$C_{18}H_{23}O_2N_3$ requires C = 69·01; H = 7·34; N = 13·41 per cent.

A solution containing 0·5002 gram in 25 c.c. of chloroform gave α_D 16°50′ in a 2-dcm. tube, whence $[\alpha]_D$ 420·6°. The semicarbazone is slowly hydrolysed by hot dilute hydrochloric acid, but is stable towards alkalis; it dissolves in concentrated sulphuric acid without rise of temperature, and, on warming, the solution develops an intense, cherry-red coloration which is destroyed on dilution, when the odour of benzaldehyde becomes perceptible.

m-*Nitrobenzaldehyde camphoryl-ψ-semicarbazone*,

$$C_8H_{14}<\begin{matrix}CH\cdot N(N{:}CH\cdot C_6H_4\cdot NO_2)\\ C(OH)\text{———————}NH\end{matrix}>CO,$$

is practically insoluble in chloroform, acetone, ether, ethyl acetate, and light petroleum ; boiling alcohol dissolves it very sparingly, depositing minute, pale yellow needles which melt at 218—220° with decomposition. It is moderately soluble in pyridine and in glacial acetic acid.

0·1214 gave 0·2681 CO_2 and 0·0723 H_2O. C = 60·23 ; H = 6·62.
$C_{18}H_{22}O_4N_4$ requires C = 60·33 ; H = 6·14 per cent.

A solution containing 0·1019 gram in 25 c.c. of pyridine gave α_D 0°10′ in a 2-dcm. tube, whence $[\alpha]_D$ 20·4° ; 0·2723 gram dissolved in 25 c.c. of glacial acetic acid gave 1°50′, whence $[\alpha]_D$ 84·1°. Unlike *m*-nitrobenzylidenesemicarbazone itself, the substance is insoluble in hot aqueous sodium hydroxide, but it dissolves in concentrated sulphuric acid, and the solution becomes orange-red when warmed.

o-*Hydroxybenzaldehyde camphoryl-ψ-semicarbazone*,

$$C_8H_{14}<\begin{matrix}CH\cdot N(N{:}CH\cdot C_6H_4\cdot OH)\\ C(OH)\text{———————}NH\end{matrix}>CO,$$

obtained from salicylaldehyde, dissolves readily in chloroform, ethyl acetate, acetic acid, and acetone, being only sparingly soluble in light petroleum, from which it crystallises in plates. When covered with cold spirit it dissolves very freely, separating almost immediately in bulky, lustrous, hydrated needles ; in this condition it softens at 206° and melts at 212°, decomposing vigorously. A specimen left in the desiccator during several weeks was found to retain approximately $\frac{1}{2}H_2O$.

0·1424 gave 0·3321 CO_2 and 0·0959 H_2O. C = 63·60 ; H = 7·48.
0·1486 „ 0·3464 CO_2 „ 0·1028 H_2O. C = 63·57 ; H = 7·68.
0·1751 „ 19·0 c.c. of nitrogen at 20° and 752 mm. N = 12·28.
$C_{18}H_{23}O_3N_3$ requires C = 65·65 ; H = 7·00 ; N = 12·76 per cent.
$C_{18}H_{23}O_3N_3,C_2H_6O$ „ C = 64·00 ; H = 7·72 ; N = 11·20 „ „
$C_{18}H_{23}O_3N_3,\frac{1}{2}H_2O$ „ C = 63·90 ; H = 7·10 ; N = 12·42 „ „

A solution containing 0·4130 gram in 25 c.c. of chloroform gave α_D 8°54′ in a 2-dcm. tube, whence $[\alpha]_D$ 269·4°, corresponding to $[\alpha]_D$ 276·8° for the anhydrous compound. After 6 hours in the steam oven, 0·1406 gram dissolved in 25 c.c. of chloroform gave α_D 3°11′, whence $[\alpha]_D$ 283·0°.

0·1001 gave 0·2402 CO_2 and 0·0622 H_2O. C = 65·44 ; H = 6·90.
$C_{18}H_{23}O_3N_3$ requires C = 65·65 ; H = 7·00 per cent.

The salicylidene-ψ-semicarbazone dissolves in alkali hydroxides and

is reprecipitated by acids; ferric chloride develops an intense, dark green coloration in alcoholic solutions.

p-*Methoxybenzaldehyde camphoryl-ψ-semicarbazone*,

$$C_8H_{14}<\begin{matrix}CH\cdot N(N:CH\cdot C_6H_4\cdot OCH_3) \\ | \\ C(OH)\text{———————}NH\end{matrix}>CO,$$

prepared from anisaldehyde, dissolves readily in benzene and in chloroform, more sparingly in acetone and in boiling alcohol, crystallising from the latter in brilliant, hexagonal plates, insoluble in ether and light petroleum; it melts and decomposes at 234°.

0·1790 gave 0·4333 CO_2 and 0·1252 H_2O. C = 66·02; H = 7·77.
$C_{19}H_{25}O_3N_3$ requires C = 66·43; H = 7·34 per cent.

A solution containing 0·4898 gram in 25 c.c. of chloroform gave α_D 17°15′ in a 2-dcm. tube, whence $[\alpha]_D$ 440·2°.

Piperonylidene camphoryl-ψ-semicarbazone,

$$C_8H_{14}<\begin{matrix}CH\cdot N(N:CH\cdot C_6H_3:O_2CH_2) \\ | \\ C(OH)\text{———————}NH\end{matrix}>CO,$$

is readily soluble in chloroform, benzene, acetone, and hot ethyl acetate, crystallising from the last-named in silky needles; hot alcohol dissolves it readily, depositing lustrous prisms which melt and decompose at 229°.

0·2031 gave 0·4711 CO_2 and 0·1179 H_2O. C = 63·26; H = 6·45.
$C_{19}H_{23}O_4N_3$ requires C = 63·87; H = 6·44 per cent.

A solution containing 0·3028 gram in 25 c.c. of chloroform gave α_D 10°54′ in a 2-dcm. tube, whence $[\alpha]_D$ 450·0°.

Vanillidene camphoryl-ψ-semicarbazone,

$$C_8H_{14}<\begin{matrix}CH\cdot N[N:CH\cdot C_6H_3(OH)\cdot OCH_3] \\ | \\ C(OH)\text{—————————}NH\end{matrix}>CO,$$

dissolves readily in organic media excepting ether and light petroleum; it exhibits a marked tendency to combine with solvents, dissolving in a small quantity of cold benzene, from which it separates immediately afterwards in crystals containing the hydrocarbon. The compound melts at 219°.

0·1765 gave 0·4345 CO_2 and 0·1144 H_2O. C = 67·15; H = 7·20.
0·2266 ,, 19·8 c.c. of nitrogen at 19° and 742 mm. N = 9·80.
0·1755 ,, 15·4 c.c. of nitrogen at 20° and 748 mm. N = 9·88.
$C_{19}H_{25}O_4N_3$ requires C = 63·51; H = 6·96; N = 11·70 per cent.
$C_{19}H_{25}O_4N_3,C_6H_6$ requires C = 68·65; H = 7·09; N = 9·61 per cent.

A solution containing 0·2268 gram in 25 c.c. of chloroform gave α_D 5°36′ in a 2-dcm. tube, whence $[\alpha]_D$ 308·6°, corresponding to $[\alpha]_D$ 375° approximately for the solvent-free compound. A specimen

crystallised from alcohol, in which it dissolves very readily, also gave results indicating the presence of the solvent.

0·1460 gave 0·3292 CO_2 and 0·0969 H_2O. C = 61·50; H = 7·37.
$C_{19}H_{25}O_4N_3,C_2H_6O$ requires C = 62·22; H = 7·65 per cent.

Cuminylidene camphoryl-ψ-semicarbazone,

$$C_8H_{14}<\begin{matrix}CH\cdot N(N{:}CH\cdot C_6H_4\cdot C_3H_7) \\ C(OH)\text{———————}NH\end{matrix}>CO,$$

prepared from cuminaldehyde, is freed from the characteristic smell of that substance with the greatest difficulty. It is readily soluble in organic media excepting ether and petroleum, and melts at 229°, when it decomposes.

0·1434 gave 0·3675 CO_2 and 0·1111 H_2O. C = 69·89; H = 8·60.
0·1862 „ 0·4744 CO_2 and 0·1433 H_2O. C = 69·48; H = 8·55.
$C_{21}H_{29}O_2N_3$ requires C = 70·99; H = 8·17 per cent.
$C_{21}H_{29}O_2N_3,C_2H_6O$ requires C = 68·82; H = 8·73 per cent.

A solution containing 0·2996 gram in 25 c.c. of chloroform gave α_D 9°20′ in a 2-dcm. tube, whence $[\alpha]_D$ 390·0°, corresponding approximately to $[\alpha]_D$ 415° for the solvent-free compound.

Cinnamylidene camphoryl-ψ-semicarbazone,

$$C_8H_{14}<\begin{matrix}CH\cdot N(N{:}CH\cdot CH{:}CH\cdot C_6H_5) \\ C(OH)\text{————————}NH\end{matrix}>CO,$$

has been examined in greater detail on account of its unusually high specific rotatory power. Twenty grams of camphorylnitroso-ψ-carbamide were reduced with zinc and dilute acetic acid, the filtered solution being treated with 10·5 grams of cinnamaldehyde, and warmed on the water-bath. The limpid oil having changed to a yellow, viscous product, the heating was discontinued, and the semicarbazone withdrawn from the liquid was rubbed with a small quantity of cold alcohol and drained on earthenware. Fifteen grams of a pale yellow powder were obtained, and on covering the dry substance with cold benzene it dissolved freely, separating immediately afterwards in crystals which dissolve sparingly in the boiling solvent; this deposited minute octahedra melting at 219° with disengagement of gas. After exposure to air during 2 hours,

0·2055 gave 0·5606 CO_2 and 0·1415 H_2O. C = 74·40; H = 7·65.
$C_{20}H_{25}O_2N_3$ requires C = 70·80; H = 7·37 per cent.
$C_{20}H_{25}O_2N_3,C_6H_6$ requires C = 74·82; H = 7·43 per cent.

A solution containing 0·2604 gram in 25 c.c. of chloroform gave α_D 8°43′ in a 2-dcm. tube, whence $[\alpha]_D$ 418·4°, corresponding to $[\alpha]_D$ 514·4° for the solvent-free compound; the residue obtained by evaporating this liquid on the water-bath gave $[\alpha]_D$ 425·0°, showing

that scarcely any benzene had been removed, whilst exposure to 100° during 3 hours raised the specific rotatory power to $[\alpha]_D$ 527·5°. Further heating appeared to racemise the substance, a specimen which originally gave $[\alpha]_D$ 418° giving $[\alpha]_D$ 483° after 12 hours in the steam oven.

Determinations of the specific rotatory power of the material having $[\alpha]_D$ 527·5° in chloroform have been made with a variety of solvents; the following results were obtained in a 2-dcm. tube, the solution in each case being made up to 25 c.c.:

0·2106 gave α_D 10°12′ in ether, whence $[\alpha]_D$ 605·4°.
0·1751 ,, α_D 4 38 in carbon disulphide, whence $[\alpha]_D$ 330·7°.
0·2011 ,, α_D 2 36 in acetone, whence $[\alpha]_D$ 161·6°.
0·2247 ,, α_D 1 55 in alcohol, whence $[\alpha]_D$ 106·6°.
0·2076 ,, α_D 1 36 in glacial acetic acid, whence $[\alpha]_D$ 96·3°.
0·2094 ,, α_D − 0 54 in pyridine, whence $[\alpha]_D$ − 53·7°.

Experiments were made also with the specimen containing benzene of crystallisation. A solution having 0·2172 gram in 25 c.c. of bromobenzene gave α_D 6°9′, whence $[\alpha]_D$ 355·9°, or $[\alpha]_D$ 437·8° for the solvent-free substance; 0·1160 gram dissolved in 20 c.c. of nitromethane gave α_D 2°54′, whence $[\alpha]_D$ 250·0° or $[\alpha]_D$ 307·5°, solvent-free: 0·2459 gram dissolved in 20 c.c. of phenetole gave α_D 9°1′, whence $[\alpha]_D$ 366·7° or $[\alpha]_D$ 451·1° for the solvent-free compound.

On allowing the solution in acetone to evaporate slowly, large, transparent, highly refractive crystals separate, but within a few seconds of withdrawing these from the mother-liquor they become opaque whilst retaining their lustre, and ultimately resemble glazed porcelain.

The cinnamylidene derivative is insoluble in light petroleum, and only moderately in ether and benzene; in the other media mentioned, it dissolves readily. A solution in concentrated sulphuric acid is deep yellow, changing to cherry-red and carmine when warmed; on diluting this liquid, the odour of cinnamaldehyde becomes noticeable.

Furfuraldehyde camphoryl-ψ-semicarbazone,

$$C_8H_{14}<\begin{matrix} CH\cdot N(N{:}CH\cdot C_4H_3O) \\ | \\ C(OH)\text{——————}NH \end{matrix}>CO,$$

separates in crystals a few moments after the aldehyde is added to a solution of camphoryl-ψ-semicarbazide in 25 per cent. acetic acid, and by recrystallisation from alcohol is obtained in aggregates of flat, transparent, rhomboidal prisms which decompose without complete fusion at 222°. The crystals become dull and opaque in the desiccator.

0·2185 gave 0·5064 CO_2 and 0·1412 H_2O. C = 63·21; H = 7·18.
$C_{16}H_{21}O_3N_3$ requires C = 63·36; H = 6·93 per cent.

A solution containing 0·1004 gram in 25 c.c. of chloroform gave α_D 4°2′ in a 2-dcm. tube, whence $[\alpha]_D$ 502·2°; 0·2301 gram dissolved in 25 c.c. of absolute alcohol gave α_D 1°51′ in the same tube, whence $[\alpha]_D$ 100·5°. The substance is insoluble in petroleum and only sparingly soluble in ether, but dissolves readily in hot alcohol, acetone, and ethyl acetate; it is freely soluble in chloroform and glacial acetic acid.

Acetone camphoryl-ψ-semicarbazone,

$$C_8H_{14}<\begin{matrix}CH\cdot N[N{:}C(CH_3)_2]\\ | \\ C(OH)\text{———}NH\end{matrix}>CO,$$

precipitated almost immediately on adding acetone to an ammoniacal solution of the *pseudo*-semicarbazide, crystallises from alcohol in lustrous needles and melts at 217° with vigorous disengagement of gas.

0·1649 gave 0·3823 CO_2 and 0·1319 H_2O. C = 63·22; H = 8·88.
$C_{14}H_{23}O_2N_3$ requires C = 63·39; H = 8·68 per cent.

A solution containing 0·1098 gram in 25 c.c. of chloroform gave $[\alpha]_D$ – 1°39′ in a 2-dcm. tube, whence $[\alpha]_D$ – 187·8°. The compound is insoluble in petroleum, and only sparingly soluble in benzene and ether; it is moderately soluble in hot alcohol and acetone, dissolving readily in ethyl acetate and chloroform.

The acetone *pseudo*-semicarbazone is indifferent towards hot alkalis, but is hydrolysed immediately by dilute hydrochloric acid, the smell of acetone being readily distinguishable in the liquid, which reduces Fehling's solution when rendered alkaline.

Camphorquinone camphoryl-ψ-semicarbazone,

$$C_8H_{14}<\begin{matrix}CH\cdot N(N{:}C_{10}H_{14}O)\\ | \\ C(OH)\text{———}NH\end{matrix}>CO,$$

obtained as a granular precipitate on warming the quinone with a solution of the *pseudo*-semicarbazide in 50 per cent. acetic acid, crystallises from boiling methyl alcohol in silky, sulphur-yellow needles and melts at 234°, when it decomposes.

0·1126 gave 0·2785 CO_2 and 0·0861 H_2O. C = 67·45; H = 8·49.
$C_{21}H_{31}O_3N_3$ requires C = 67·56; H = 8·31 per cent.

A solution containing 0·2354 gram in 25 c.c. of chloroform gave α_D – 5°55′ in a 2-dcm. tube, whence $[\alpha]_D$ – 314·2°. The substance is insoluble in petroleum, and only very slightly soluble in boiling benzene, but it dissolves with moderate readiness in boiling acetone, ethyl acetate, methyl alcohol, and ethyl alcohol.

Benzoquinone camphoryl-ψ-semicarbazone,

$$C_8H_{14}<\begin{matrix}CH\cdot N(N{:}C_6H_4O)\\ | \\ C(OH)\text{———}NH\end{matrix}>CO,$$

separates in shimmering brown leaflets on warming for a few moments the dark red liquid obtained when benzoquinone is dissolved by a solution of the *pseudo*-semicarbazide in 50 per cent. acetic acid; it crystallises from boiling methyl alcohol in lustrous, golden-brown needles with faint violet reflex, and melts at 197°, when it decomposes.

0·1364 gave 0·3221 CO_2 and 0·0829 H_2O. C = 64·40; H = 6·75.
0·1195 ,, 14·5 c.c. of nitrogen at 20° and 746 mm. N = 13·32.
$C_{17}H_{21}O_3N_3$ requires C = 64·76; H = 6·66; N = 13·33 per cent.

The substance is insoluble in boiling petroleum, dissolving very sparingly in boiling benzene and warm ether; it is moderately soluble in cold glacial acetic acid, hot acetone, and hot ethyl acetate, whilst pyridine dissolves it freely. A determination of the solubility in chloroform showed that one gram requires about 2500 c.c. of the cold solvent.

A solution containing 0·1018 gram in 20 c.c. of pyridine gave α_D − 10°42′ in a 2-dcm. tube, whence $[\alpha]_D$ − 1051°, which follows also from α_D − 2°50′, given by 0·1011 gram dissolved in 75 c.c. of acetone; 0·0164 gram in 50 c.c. of chloroform gave α_D − 0°42′, whence $[\alpha]_D$ − 1067°, and a solution containing 0·0233 gram in 25 c.c. of absolute alcohol gave α_D − 1°1′, whence $[\alpha]_D$ − 545°.

The Anhydride of Camphoryl-ψ-semicarbazide, $C_8H_{14}<$ CH—N, NH, C—NH $>CO$.

On obtaining camphoryl-ψ-semicarbazide for the first time, about twelve months ago, we believed it to have the normal constitution corresponding to methylsemicarbazide, $NH_2·N(CH_3)·CO·NH_2$, and accordingly endeavoured to prepare from it the unknown camphorylhydrazine, $C_{10}H_{15}O·NH·NH_2$, in the manner by which von Brüning obtained methylhydrazine from nitrosomethylcarbamide (*Annalen*, 1889, **253**, 7). Camphorylnitroso-ψ-carbamide was therefore reduced with zinc and acetic acid, the solution of *pseudo*-semicarbazide being filtered, evaporated to small bulk, and heated with excess of concentrated hydrochloric acid during 8 hours in a reflux apparatus; on driving off the excess of hydrochloric acid and diluting largely with water, a precipitate was obtained which, after crystallisation from alcohol, could be sublimed in minute, silky threads resembling philosopher's wool. If the substance is fused on a spatula and allowed to return to the temperature of solidification, a woolly cluster of silky threads suddenly covers the solid.

0·1920 (sublimed) gave 0·4504 CO_2 and 0·1454 H_2O. C = 63·98; H = 8·41.

0·1045 (sublimed) gave 18·5 c.c. nitrogen at 25° and 770 mm. N = 20·58.

0·1660 (unsublimed) gave 0·3878 CO_2 and 0·1238 H_2O. C = 63·71; H = 8·40.

$C_{11}H_{17}ON_3$ requires C = 63·77; H = 8·21; N = 20·29 per cent.

The sublimed anhydride melts at 280° and is moderately soluble in alcohol, from which it crystallises in silky needles; it dissolves in concentrated hydrochloric acid and is precipitated on dilution. It is sparingly soluble in cold chloroform, acetone, ethyl acetate, and boiling benzene, more readily in glacial acetic acid, but is insoluble in cold benzene and petroleum. Fehling's solution has no action on it, and attempts to methylate and benzoylate the substance were unsuccessful.

The specimen obtained in the manner described appears to have become racemised, a solution containing 0·1123 gram in 25 c.c. of chloroform giving α_D − 0°50′ in a 2-dcm. tube, whence $[\alpha]_D$ − 92·7°; a more highly active product, however, has been obtained by hydrolysing the acetone-ψ-semicarbazone with hydrochloric acid, and crystallising the product from alcohol, which deposited hard, lustrous plates melting at 276°.

0·1950 gave 0·4528 CO_2 and 0·1477 H_2O. C = 63·33; H = 8·41.

0·1675 ,, 30·2 c.c. nitrogen at 20° and 766 mm. N = 20·30.

$C_{11}H_{17}ON_3$ requires C = 63·77; H = 8·21; N = 20·29 per cent.

A solution containing 0·1011 gram of this specimen in 20 c.c. of chloroform gave α_D − 1°53′ in a 2-dcm. tube, whence $[\alpha]_D$ − 186·2°. On heating this specimen with hydrochloric acid on the water-bath during 24 hours, the specific rotatory power fell to $[\alpha]_D$ − 181·5°, indicating slight racemisation; it was not expected that the low figure of the first preparation would be reached, because that material had been in contact with moderately strong hydrochloric acid during six months.

Substituted α-Camphylcarbamides.

The production of two isomeric carbamides from α-aminocamphor (this vol., p. 110) led us to study the action of cyanic acid on α-camphylamine, the unsaturated base obtained by reducing α-campholenonitrile with sodium and alcohol, first by Goldschmidt and Schulhoff (*Ber.*, 1886, **19**, 709) and later by Tiemann (*Ber.*, 1896, **29**, 3006). Although this base is converted readily into the normal carbamide derivative when the hydrochloride is mixed with potassium cyanate,

our attempts to prepare an isomeride corresponding to camphoryl-ψ-carbamide have been unsuccessful.

By the action of nitrous acid on the carbamide, α-camphylcarbimide has been obtained in the form of an oil with a penetrating odour, but distillation causes it to decompose violently; nevertheless, its chemical nature is clearly established by the production of substituted carbamides from interaction with primary bases.

α-Camphylcarbamide, $C_{10}H_{17}\cdot NH\cdot CO\cdot NH_2$.

Fifty grams of α-camphylamine were dissolved in 1700 c.c. of water containing 75 c.c. of concentrated hydrochloric acid, and treated with a solution containing 75 grams of potassium cyanate in 200 c.c. of water; in the course of 2 hours, a considerable amount of the carbamide had separated in felted needles, and, a further 20 grams of potassium cyanate having been added, action was allowed to proceed during 12 hours. After recrystallisation from dilute alcohol, the compound melted at 110°.

0·1011 gave 0·2492 CO_2 and 0·0949 H_2O. C = 67·22; H = 10·43.
$C_{11}H_{20}ON_2$ requires C = 67·34; H = 10·20 per cent.

The carbamide is insoluble in petroleum, but dissolves very readily in alcohol, chloroform, and benzene, separating immediately from the last-named solvent in the form of a jelly, which becomes crystalline in the course of 24 hours; this property is due to association with the hydrocarbon, thus recalling the behaviour of the camphorylcarbamides. It does not reduce Fehling's solution.

All attempts to produce a nitroso-derivative or to convert the carbamide into an isomeric substance corresponding to camphoryl-ψ-carbamide having failed, we regard the compound as having the normal structure of a substituted urea, and as being incapable of existence in the *pseudo*-form.

α-Camphylcarbimide, $C_{10}H_{17}\cdot N\colon C\colon O$.

Twenty-five grams of α-camphylcarbamide were suspended in 400 c.c. of water to which 60 c.c. of hydrochloric acid had been added, the substance dissolving almost entirely; crystals of sodium nitrite were then added to the uncooled liquid until the green colour at first developed had disappeared, nitric oxide being then liberated. Meanwhile, there separated an oil having an overpowering, tear-exciting odour, surpassing those of camphorylcarbimide and bornylcarbimide in disagreeable qualities; this product was collected with ether, dried with calcium chloride, and heated in a distilling flask, but on reaching the boiling point violent effervescence ensued, a portion of the material

being shot out of the flask, whilst the remainder became solid. On repeating the preparation, the oil was distilled in steam, which converted about one-half into dicamphylcarbamide, allowing the other to pass over; this specimen was converted into the following derivatives, readily obtained in each case by the action of the corresponding base dissolved in benzene.

s-*Camphylpiperidylcarbamide*, $CO<^{NH\cdot C_{10}H_{17}}_{N\cdot C_5H_{10}}$, crystallises from a mixture of benzene and petroleum in leaflets melting at 118°.

0·0884 gave 0·2344 CO_2 and 0·0848 H_2O. C = 72·32; H = 10·66.
$C_{16}H_{28}ON_2$ requires C = 72·72; H = 10·60 per cent.

s-*Camphylphenylcarbamide*, $CO<^{NH\cdot C_{10}H_{17}}_{NH\cdot C_6H_5}$, separates from dilute alcohol in needles melting at 120—121°.

0·1141 gave 0·3129 CO_2 and 0·0940 H_2O. C = 74·79; H = 9·15.
$C_{17}H_{24}ON_2$ requires C = 75·00; H = 8·83 per cent.

s-*Camphyl*-p-*tolylcarbamide*, $CO<^{NH\cdot C_{10}H_{17}}_{NH\cdot C_6H_4\cdot CH_3}$, crystallises from dilute alcohol in stellate groups of long, slender needles melting indefinitely at 135°.

0·1596 gave 0·4406 CO_2 and 0·1327 H_2O. C = 75·29; H = 9·24.
$C_{18}H_{26}ON_2$ requires C = 75·52; H = 9·09 per cent.

s-*Dicamphylcarbamide*, $CO(NH\cdot C_{10}H_{17})_2$, remains in the flask from which camphylcarbimide has been distilled with steam; it crystallises from alcohol in slender, lustrous needles melting somewhat indefinitely at 153—154°.

0·1035 gave 0·2888 CO_2 and 0·1006 H_2O. C = 76·09; H = 10·80.
$C_{21}H_{36}ON_2$ requires C = 75·91; H = 10·84 per cent.

These derivatives of camphylamine are not sufficiently interesting to invite further investigation, but the study of camphoryl-ψ-semicarbazide is being continued.

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LXXIV.—*Estimation of Potassium Permanganate in the presence of Potassium Persulphate.*

By John Albert Newton Friend, M.Sc.

It is well known that persulphates liberate iodine from potassium iodide (Marshall, *Proc. Roy. Soc. Edin.*, 1898, **22**, 388). In fact, this reaction affords a method for their quantitative estimation (*Chem. Zeit.*, 1899, **23**, 699). If, however, dilute solutions of both are employed, the iodine is liberated very slowly. A series of experiments has been carried out in order to determine whether the presence of small quantities of persulphate would interfere with the iodometric estimation of potassium permanganate in dilute solution, the results of which are indicated below.

1. *Concentration of Iodide.*

The permanganate solution was freshly prepared each day (Gardner and North, *J. Soc. Chem. Ind.*, 1904, **23**, 599) by dissolving the crystals in cold water. Portions of the solution were acidified, mixed with persulphate solution, and diluted to 150 c.c. Varying quantities of potassium iodide solution were then added, and after standing for one minute the liberated iodine was estimated by titration with *N*/100 sodium thiosulphate, which had been made several days previously (Dupré, *Zeit. angew. Chem.*, 1904, **17**, 815). Fresh starch solution was used as indicator, and the sulphuric acid was approximately 1/10 molecular.

In the following series:

Column I gives the number of grams of persulphate in solution.

Column II gives the titration in c.c. of thiosulphate when just sufficient iodide had been added to reduce the permanganate.

Columns III, IV, V, and VI give, respectively, the titrations when twice, three times, four times, and six times the equivalent of iodide had been added.

Series I.

I.	II.	III.	IV.	V.	VI.
0·00 gram	19·41 c.c.	19·41 c.c.	19·41 c.c.	19·41 c.c.	19·41 c.c.
0·02 ,,	19·36 ,,	19·41 ,,	19·44 ,,	19·42 ,,	19·47 ,,
0·04 ,,	19·38 ,,	19·41 ,,	19·41 ,,	19·43 ,,	19·48 ,,
0·06 ,,	19·40 ,,	19·40 ,,	19·49 ,,	19·48 ,,	19·50 ,,
0·08 ,,	19·38 ,,	19·41 ,,	19·49 ,,	19·48 ,,	19·53 ,,
0·10 ,,	19·41 ,,	19·49 ,,	19·50 ,,	19·53 ,,	19·60 ,,

The foregoing results show that the concentration of the iodide has a slight but decided effect on the titrations, the most accurate results being obtained when only a slight excess of iodide is used.

2. *Concentration of Acid.*

The results obtained by varying the concentration of the sulphuric acid are given in Series II.

Column I gives the concentration of the acid.*

Columns II, III, and IV give the titrations with $N/100$ thiosulphate in the presence of 0·04 gram, 0·06 gram, and 0·08 gram of persulphate respectively.

As before, the solutions were diluted to 150 c.c. before titration, and only a very slight excess of iodide was added.

Series II.

H_2SO_4.	$K_2S_2O_8$, 0·04 gram.	$K_2S_2O_8$, 0·06 gram.	$K_2S_2O_8$, 0·08 gram.
$M/18$	19·42 c.c.	14·94 c.c.	14·97 c.c.
$M/9$	19·41 ,,	14·96 ,,	14·99 ,,
$M/6$	19·41 ,,	14·99 ,,	15·00 ,,
$M/3$	19·40 ,,	15·00 ,,	15·00 ,,
Theoretical values	19·41 ,,	14·95 ,,	14·95 ,,

The concentration of the acid has but little effect when the amount of persulphate is small. The most accurate results are obtained, however, when the acidity is reduced to a minimum (compare Trans., 1904, **85**, 601).

From the foregoing results, it appears that correct titrations may be obtained if (1) only a slight excess of iodide is added; (2) but little acid is present.

That such is the case will be evident from a consideration of the following data.

Column I gives the number of grams of persulphate.

Column II gives the titration in c.c. of $N/100$ thiosulphate.

Column III gives the theoretical titration, that is, the titration obtained when no persulphate is present. The volume titrated was 160 c.c., the concentration of acid being approximately 1/20-molecular.

Series III.

I.	II.	III.	I.	II.	III.
0·02 gram	13·54 c.c.	13·50 c.c.	0·06 gram	13·54 c.c.	13·50 c.c.
0·02 ,,	14·98 ,,	14·96 ,,	0·06 ,,	14·95 ,,	14·96 ,,
0·02 ,,	15·55 ,,	15·54 ,,	0·06 ,,	15·53 ,,	15·54 ,,
0·02 ,,	16·00 ,,	16·00 ,,	0·06 ,,	16·00 ,,	16·00 ,,
0·04 ,,	13·48 ,,	13·50 ,,	0·08 ,,	13·51 ,,	13·50 ,,
0·04 ,,	14·95 ,,	14·96 ,,	0·08 ,,	14·98 ,,	14·96 ,,
0·04 ,,	15·51 ,,	15·54 ,,	0·08 ,,	15·56 ,,	15·54 ,,
0·04 ,,	15·99 ,,	16·00 ,,	0·08 ,,	16·01 ,,	16·00 ,,

* M = molecular weight in grams per litre.

Conclusion.—If proper precautions are taken, small quantities of potassium permanganate may be estimated iodometrically in the presence of any weight of potassium persulphate not exceeding 0·08 gram.

THE GRAMMAR SCHOOL,
WATFORD.

LXXV.—*The Purification of Water by Continuous Fractional Distillation.*

By WILLIAM ROBERT BOUSFIELD, M.A., K.C., M.P.

THE method generally used in preparing water of a high degree of purity is that which was introduced by Stas in the course of his atomic weight determinations. The organic matter in the water is oxidised by distilling successively with strong and with dilute alkaline permanganate (Stas used the manganate), and the ammonia produced by the oxidation is removed by distilling a third time with potassium hydrogen sulphate. Whilst ordinary good distilled water has a conductivity of some 5 to 10 reciprocal megohms per centimetre cube, it is possible, by Stas' method under favourable conditions, to obtain water having a conductivity of barely one of these units.*

Kohlrausch has recently shown that the conductivity of water purified by Stas' method may be further reduced from 0·9 to 0·5 by keeping it in contact with an atmosphere freed from carbon dioxide by means of lime (*Zeit. Physikal. Chem.*, 1902, **42**, 193). A somewhat remarkable further purification took place when water, freed from carbon dioxide in this way, was acted on by a current of purified air while in contact with platinum electrodes. The platinum black, saturated with oxygen, appears to oxidise the volatile organic impurities, and the carbon dioxide produced is carried off by the current of air. Any ammonia that might be present is probably oxidised to nitrogen and water. This further purification reduces the conductivity of the water to 0·2 to 0·3 gemmhos, and although this value is five times as great as that recorded by Kohlrausch and Heydweiler for water purified in a vacuum (*Wied. Annalen*, 1894, **53**, 209), it is nevertheless too

* The suggestion that the names for the units of conductivity should be derived by reversing the names of the corresponding units of resistance is due to Lord Kelvin. For many purposes the reciprocal megohm is a more convenient unit of conductivity than the reciprocal ohm, and Prof. Ayrton has suggested that it may conveniently be described as a "gemmho."

pure to be easily preserved, and unless special precautions are adopted it soon reverts to the normal conductivity of water, purified in contact with the atmosphere.

With the object of testing how far the purification of water could be carried by redistillation, an apparatus was some time ago constructed by the author, in which two platinum tubes were suspended over platinum cups in an exhausted receiver, the two tubes being cooled internally by the circulation of water. They thus served as condensers, so that the condensed water ran down into the platinum cups, and its conductivity could be measured between tube and cup as electrodes. The water overflowed the cups and was thus redistilled continuously. The water circulation passed from one tube to the other, so that there was a slight difference of temperature between the condensing tubes, one being at about 18° and the other at about 20°. This apparatus did not give the anticipated results, but, incidentally, an important observation was made which led to the construction of the still which is the subject of this paper. It was observed that the cooler tube always condensed the purer water, as measured by its conductivity, which suggested the presence of a volatile organic impurity having a slightly higher boiling point than water, and the possibility of separating such impurity on a practical scale by a process of fractionation depending on the use of surfaces of different temperatures.

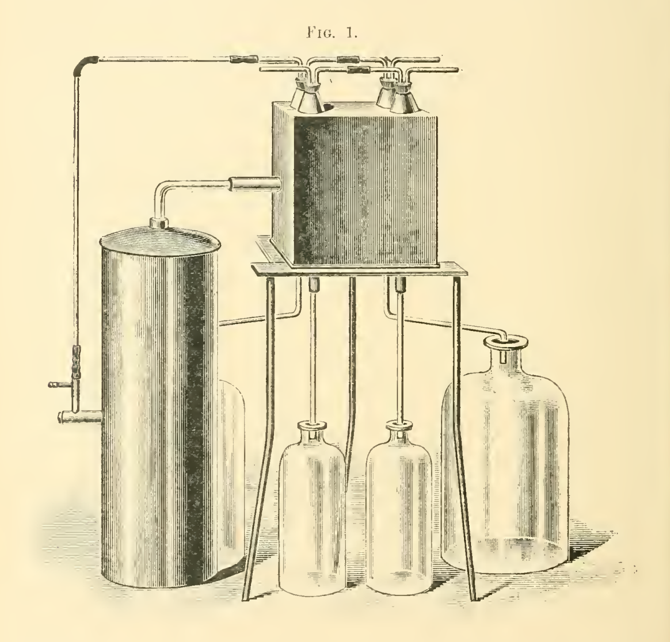
The production of water of a high degree of purity for conductivity work with dilute solutions is a matter of great importance, and the object of the still which forms the subject of the present communication is to effect, by a single continuous operation, the preparation of large quantities of water having a conductivity not greatly exceeding one gemmho, a value that may be taken as typical of a thoroughly good sample of conductivity water. This result has been achieved by a process of fractional distillation, in which water is continuously distilled and fractionally condensed on surfaces differing in temperature and in the material of which they are constructed. As is indicated below, this method of purification has been found, without any preliminary purification, to produce water at least equal in purity to that prepared by the three operations of Stas' method. The still can be run continuously day and night, and it is possible to collect every twenty-four hours some ten litres, with no further trouble than that necessitated by the occasional cleaning of the still.

EXPERIMENTAL.

The apparatus consists of two parts, a still and a condenser, and the general arrangement of these is shown in Fig. 1.

(1) The *still*, shown in section in Fig. 2, was specially designed to prevent particles of spray from being carried over with the steam. The copper cylinder which forms the boiler is furnished with a branch-pipe, A, and the water to be distilled is fed con-

FIG. 1.

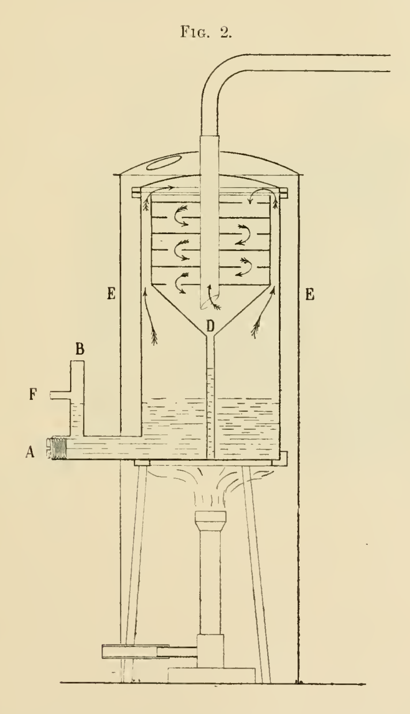


tinuously into the opening, B, the excess of water escaping at F. The circulating water from the hottest condensing tube is used for the feed water. The steam ascending from the boiling water passes upwards to the top of the cylinder, then down through holes in a series of baffle-plates, and finally upwards through a central tube, from which it is delivered to the condenser. The spray, which is driven against the baffle-plates, runs down the sides of the funnel D and back into the water below. An external covering, E E, of

galvanised sheet iron, serves to economise the heat of the burner, and helps also to dry the steam.

(2) The *condenser* shown in Fig. 3 consists of a box of sheet copper with a lid, which has four openings with inclined sides. These openings serve to support four glass test-tubes, cooled by circulating water. Through two of the test-tubes, a rapid flow of water passes, and from these the best water is collected by means

FIG. 2.

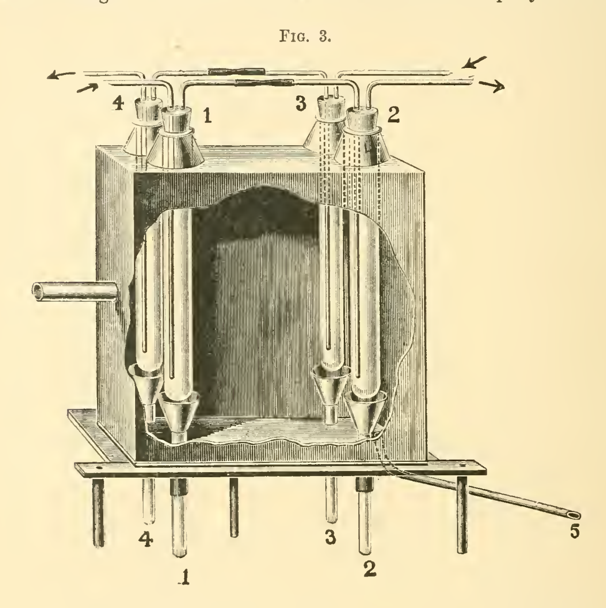


of the glass funnels 1 and 2. Through the other tubes water passes very slowly, becoming finally heated to 60° to 80°; this water is used to feed the still, and serves also to condense a small quantity of distilled water, which is collected by the funnels 3 and 4; this distilled water has a higher conductivity and is of poorer quality than that collected from the cold tubes by the funnels 1 and 2. About one-third of the water distilled condenses on the surface of

the copper box, and is collected from the copper tube 5. The arrangement of the tubes is usually that shown in Fig. 3, the steam from the still being delivered from a glass tube against the further wall of the copper box directly above the tube 5.

(3) *The Water.*—The conductivity of the water produced depends to some extent on the conditions under which the still is used. When using the water of the West Middlesex Company in the

FIG. 3.



author's laboratory at Hendon, typical values for the five samples were—

	1.	2.	3.	4.	5.
κ_{18} =	1·2	1·2	1·9	4	4 gemmhos.

With slightly different conditions, values obtained were—

	1.	2.	3.	4.	5.
κ_{18} =	1·1	1·2	1·3	1·6	7 gemmhos.

The addition of alkali to the water in the still in order to hold back carbon dioxide was found to be an advantage, but a more marked improvement on these numbers was obtained by adding potassium hydrogen sulphate in order to hold back ammonia and

basic impurities. Although the distillate was not wholly free from ammonia, all the fractions were found to have a very low conductivity, as is shown by the two series—

	1.	2.	3.	4.	5.
κ_{18} =	1·0	1·0	0·96	1·3	3·0 gemmhos.
κ_{18} =	1·1	1·6	1·1	—	3·1 ,,

Under these conditions, the normal product of the coolest tube of the still is gemmho-water, and this can be produced in any desired quantity by the method now described. By storing this water in a large bottle in contact with air freed from carbon dioxide by means of lime, its conductivity can be reduced to 0·75, and a further improvement can be effected by boiling, as described on p. 746.

When a duplicate still was installed in one of the chemical laboratories at the Central Technical College, South Kensington, the average conductivity of the five samples was—

	1.	2.	3.	4.	5.
κ_{18} =	1·7	2·3	5		15 to 20 gemmhos.

Although these values are inferior to those recorded above, they were nevertheless more favourable than those obtained by Stas' method under the same conditions. At the end of three successive distillations from potassium permanganate and acid sulphate, finally through a silver tube, the conductivity of the water did not fall below 2 to 3 gemmhos, and the product was thus inferior to that separated in a single operation by continuous fractional distillation. To prepare gemmho-water in the atmosphere of a chemical laboratory is, in any case, a somewhat difficult task, and Stas' method was found to have no advantage over the continuous process described above.

Although the quantity of water condensed on the hottest test tubes is always small, its presence seems to be essential for the successful working of the still, and a large increase in the copper condensing surface was found inadequate to compensate for the removal of these tubes.

The relative purity of the different samples of water is considerably varied by varying the rate of flow of the condensing water. It is usually convenient to make the rate of flow through tubes 3 and 4 just sufficient to supply a slight excess of feed water for the still. Under these conditions, the quality of water condensed in tube 4 is greatly inferior to the product of tube 3. If this rate of flow is increased, the quantity and quality of the product of tube 4 are increased, slightly at the expense of all the other tubes.

It is the author's practice, each morning and night when the still is working, to test the product of each tube by taking its

conductivity and to pour off the water into a series of large stock-bottles, which are graduated according to conductivities. With the accumulation of impurities in the still, the quality of the product deteriorates, and if the still is running continuously it should be cleared of slime through the opening A, and washed out through the same opening every two or three days.

(4) *Glass versus Platinum.*—In the final stage of Stas' process, it is usually considered desirable to use a platinum condenser. The fouling produced by bringing purified water into contact with glass is undoubtedly serious when soft glass is used, especially when the volume of water is small or the temperature high. The difficulties arising from the solubility of glass have, however, been greatly over-estimated, and contact with the atmosphere appears to be by far the most serious cause of fouling in the case of purified water. In this connection it is of interest to note that the best water that has yet been prepared (Kohlrausch and Heydweiler, *loc. cit.*) was purified in a glass vessel, but isolated from the atmosphere by exhausting and sealing. In purifying water by continuous fractional distillation, no marked advantage is derived by using condensing tubes of platinum in place of glass. When two of the glass test-tubes and funnels were replaced by platinum, better water was obtained from cold glass tubes in positions 1 and 2, and hot platinum tubes in positions 3 and 4, than with the converse arrangement.

Although no advantage is derived from condensing the purified water on platinum tubes, a very great improvement results when the purified water is boiled for a few minutes in a platinum bottle. By this process, the conductivity may be reduced by as much as 50 per cent., and the reduction in conductivity is proportionately greatest in the case of the purest samples of water. The water purified by boiling usually has a conductivity of about 0·8, but samples of a conductivity as low as 0·6 have been obtained. In one instance, a sample of water that had an initial conductivity 0·84 at 18° was reduced by boiling for two minutes to 0·48; this low conductivity represents an exceptionally high degree of purification, and has, it is believed, only been excelled by Kohlrausch in the two series of experiments cited in the earlier portion of the paper.

(5) *Ammonia Determinations.*—Although the still was designed primarily for the preparation of purified water for conductivity measurements, it can also be used for preparing ammonia-free water. A considerable number of ammonia determinations have been made, and the proportion of ammonia in the different samples has been found to correspond roughly with their electrical con-

ductivity. An exception is found in the case of the water condensed on copper surfaces, which has a higher conductivity than might be expected from its content of ammonia. This high conductivity may be due either to non-volatile impurities carried over as spray from the still, or to metallic impurities derived from the copper box. The following table shows the relationship between the electrical conductivity and the proportion of ammonia in two series of samples prepared with the help of potassium hydrogen sulphate:

	κ_{18}.	Ammonia.	κ_{18}.	Ammonia.
1.	1·0	0·001	1·1	None
2.	1·0	0·001	1·6	Trace
3.	0·96	0·007	1·1	0·001
4.	1·3	0·007	—	—
5.	3 0	0·004	3·1	0·005

In the first series, the hot tubes (3 and 4) were of platinum and the cold tubes of glass; in the second series, this arrangement was reversed. The whole of the ammonia in the distilled water, expressed in parts per 100,000 in the above table, was in the "free" state, but before distillation the ammonia, amounting altogether to barely 0·001/100,000, was for the most part combined.

The thanks of the author are due to Dr. T. M. Lowry, under whose care the still at the Central Technical College was installed, and who supplied the data obtained from the use of the still at the College, and also made the foregoing ammonia determinations.

LXXVI.—*The Influence of the Hydroxyl and Alkoxyl Groups on the Velocity of Saponification. Part I.*

By Alexander Findlay and William Ernest Stephen Turner, M.Sc.

Although many investigations have been undertaken for the purpose of obtaining some insight into the influence of constitution on the velocity of ester formation under the influence of mineral acids, more especially in the case of the substituted benzoic and acetic acids (Menschutkin, Victor Meyer, Meyer and Sudborough, Goldschmidt, Kellas, Sudborough and Lloyd, Wegscheider, and others), comparatively little systematic work has been done on the rate of saponification of esters by alkalis as affected by constitution. In the case of esterification of acids in presence of hydrochloric acid, it was found that substitution diminishes, in every case, the velocity of esterification, and this influence is specially prominent in the case of the

ortho-substituted benzoic acids. In all such cases, it is apparently the mass, not the chemical nature of the substituent, that is of importance. The retarding influence of substitution, however, is observed not only in the case of the substituted benzoic acids, but also in the case of the substituted acetic acids (Sudborough and Lloyd, Trans., 1898, **73**, 81; 1899, **75**, 467).

Whilst with regard to hydrolysis by hydrochloric acid the general rule applies that esters which are formed with difficulty under the influence of hydrochloric acid are also hydrolysed with difficulty (V. Meyer, *Ber.*, 1895, **28**, 1262; compare Kistiakowsky, *Zeit. physikal. Chem.*, 1898, **27**, 250), the same does not apply to saponification with alkali (compare Kellas, *Zeit. physikal. Chem.*, 1897, **24**, 243; van Dyken, *Rec. Trav. chim.*, 1895, **14**, 106). In this case, the effect of substitution varies with the nature of the substituent. Thus, whilst substitution of hydrogen by alkyl groups in acetic acid diminishes the velocity of saponification, replacement of hydrogen by halogens increases the velocity of saponification (Sudborough and Feilman, *Proc.*, 1897, **13**, 241). Although, in these cases, the velocity of saponification increases with the strength of the acid, other cases are known where this is not so; as, for example, in the case of the saponification of the esters of the substituted malonic acids (Hjelt, *Ber.*, 1896, **29**, 110; 1864, **31**, 1844). There are other factors, therefore, such as steric influences, affecting the velocity of saponification of an ester, and if the effect of different substituting groups be studied, it can easily happen that the steric influences may counterbalance or overbalance the influence of the particular substituting group on the strength of the acid. To determine in how far ease of saponification of an ester runs parallel with the strength of the acid from which it is formed, it will be necessary to eliminate the steric influences as far as possible, and to study the effect of introduction of some particular substituent on the strength of different acids and the rate of saponification of the esters derived from them.

As no measurements have yet been made of the effect of the hydroxyl group on the velocity of saponification of esters of the fatty series, we resolved to study this, as well as the effect of substituting the hydrogen of the hydroxyl group. The results of the first measurements in this direction are given in the present communication.

That the introduction of the hydroxyl group into an ester greatly increases the velocity of saponification is well known. One need only refer to the ready saponifiability of ethyl lactate as compared with that of ethyl propionate. The quantitative influence of this substitution has also been obtained indirectly in the case of the enolic form of ethyl acetoacetate (Goldschmidt, *Ber.*, 1900, **33**, 1150). As the velocity of saponification of the esters of lactic acid is too great to be

measurable, we chose for investigation the esters of mandelic acid, on which measurements can be made, although with difficulty. Measurements were carried out not only in aqueous solution (except in the case of ethyl phenylpropoxyacetate, which is too sparingly soluble), but also in 30 and 60 per cent. alcohol reckoned by weight. The temperature was 25° in all cases; for although the ready saponifiability of the esters made it advisable to work at a lower temperature, the sparing solubility of some of the esters rendered this course impossible.

In carrying out the measurements, 10 c.c. of the reaction mixture were run into excess of standard hydrochloric acid, and the excess of acid titrated with a solution of caustic soda. Since the velocity of the reaction is so great, an error in the determination of the time of mixing and of stopping the reaction becomes somewhat serious. We sought to diminish this as far as possible by noting the time occupied in mixing the solutions, as well as that required for the pipette to deliver, and the mean point of these intervals was taken as the time at which the reaction was started or stopped. The saponification constant was calculated by the usual formula for a reaction of the second order, $k = \frac{2 \cdot 302 \times 10}{T_\infty Nt} \log \frac{T_t(T_0 - T_\infty)}{T_0(T_t - T_\infty)}$.

The values of the saponification constants in aqueous solution are as follows (see Tables 1—6):

Ester.	k.	Ester.	k.
Ethyl phenylacetate	12·4	Ethyl phenylmethoxyacetate...	23·3
Methyl mandelate	157	Ethyl phenylethoxyacetate ...	15·7
Ethyl mandelate	66	Ethyl phenylpropoxyacetate ...	(13·3)
Propyl mandelate	55		

In the case more especially of methyl mandelate, the velocity of saponification is so great that more than half the reaction had taken place during the first minute, so that only the second half—in the case of the stronger solutions only the last third—of the reaction could be measured. This fact introduces some uncertainty into the results, but it is evident from the agreement between the results of different experiments at different concentrations that the values obtained for the saponification constants are in any case fairly approximate.

The numbers in the foregoing table show at once the greatly accelerating influence which the hydroxyl group exercises on the velocity of saponification of ethyl phenylacetate, the saponification constant being increased to more than five times its previous value. With this we may compare the influence of the hydroxyl group on the affinity constants of the acids. Whereas the affinity constant of phenylacetic acid is 0·00502, that of mandelic acid is 0·0417, or about eight times as great.

On replacing the hydrogen of the hydroxyl group by an alkyl substituent, the velocity of saponification is greatly diminished, and the diminution increases with increase in the mass of the alkyl group. In the case of ethyl phenylpropoxyacetate, the saponification velocity could not be determined in aqueous solution on account of the sparing solubility of the ester. The number given in the foregoing table was calculated as follows: the saponification constant of ethyl phenylmethoxyacetate in 60 per cent. aqueous alcoholic solution was taken as being 7·97 (Table 17), and that for ethyl phenylpropoxyacetate, 4·77 (Table 19). Since the saponification constant of ethyl phenylmethoxyacetate in aqueous solution is 23·3, then, if the influence of the alcohol in the solution is the same on the saponification of the proproxy- as of the methoxy-ester, the saponification constant of the former in aqueous solution should be $\frac{4{\cdot}77 \times 23{\cdot}3}{7{\cdot}97} = 13{\cdot}9$. In the same way, from the numbers for ethyl phenylethoxyacetate (Table 18), the value of the saponification constant was calculated to be 12·7. As the mean of the two numbers, 13·3 was taken; it can, however, be regarded only as approximate.

If we take this value for the saponification constant of ethyl phenylpropoxyacetate as approximately correct, we find that the effect of increase in the mass of the alkyl group is a regular one, the ratios between the constants for ethyl mandelate and for ethyl phenylmethoxyacetate, ethyl phenylethoxyacetate and ethyl phenylpropoxyacetate respectively being very nearly 2·8 : 1, 3 8 : 1, 4·8 : 1. The comparison between the velocities of saponification and the affinity constants of the acids from which they are derived cannot yet be made, but we hope soon to be in a position to do so.

The influence of substitution on saponification can also be readily seen by comparing the substituted esters with the esters of acetic acid. In the following table, the values of the saponification of methyl and propyl acetates have been calculated from the figures obtained by Reicher (*Annalen*, 1885, **228**, 257), whilst that for ethyl acetate was determined by Messrs. Schmidt (*Ber.*, 1899, **32**, 3396):

Ester.	k.	Ester.	k.
Methyl acetate	9·66	Methyl mandelate	157
Ethyl acetate	6 94	Ethyl mandelate	66
Propyl acetate	5·31	Propyl mandelate	55
		Ethyl phenylacetate	12·4

From this table, it is seen that the velocity constants of the mandelates are about 10 times, in the case of methyl mandelate about 16 times, as great as those for the corresponding acetates. This increase in the saponification constant is, of course, due to

two substitutions; firstly, to substitution of hydrogen by the phenyl group, which raises the saponification constant of the ethyl ester from 6·94 to 12·4, or by nearly 1·8 times; and secondly, to introduction of the hydroxyl group, which further increases the velocity constant 5·3 times. If, now, it is assumed that a given substitution always produces the same relative increase in the saponification constant of an ester, just as one finds it to do so approximately in the case of the affinity constants of acids (Wegscheider, *Monatsh.*, 1902, **23**, 289), one should be able to calculate the value of the saponification constants of methyl and propyl mandelates from the value of the constants for the corresponding acetates. In this way one obtains, for methyl mandelate, $9{\cdot}66 \times 1{\cdot}8 \times 5{\cdot}3 = 92$ (instead of the experimentally determined value 157), and for propyl mandelate, $5{\cdot}31 \times 1{\cdot}8 \times 5{\cdot}3 = 51$ (instead of the experimental value 55). From this it will be seen that whilst the saponification constants of the ethyl and propyl esters are equally affected by the substitutions, the methyl ester is affected to a much larger degree. As we do not possess the value of the saponification constant of methyl phenylacetate, it is not possible to say whether the abnormal influence of the substituent is found in both stages of the substitution between methyl acetate and mandelate, or only in one.

In the hydrolysis of esters under the influence of acids, it has been shown (compare Hemptinne, *Zeit. physikal. Chem.*, 1894, **13**, 389; Loewenherz, *ibid.*, **15**, 561) that the ratio of the hydrolysis constants of the methyl and ethyl and of the ethyl and propyl esters of the fatty acids is constant, no matter what the acid is. When one compares the saponification constants of the esters of acetic and mandelic acids, it is found that whilst the ratio of the constants for the ethyl and propyl esters is the same, namely, 6 : 5, there is no agreement between the ratios for the methyl and ethyl esters. Thus in the case of the acetates, the ratio of the constants is approximately 3 : 2, and in the case of the mandelates 4·8 : 2. Although it is not impossible that a portion of this deviation may be due to inaccuracy in the determination of the saponification constant of methyl mandelate, we do not think that the whole of the deviation can be thus accounted for.

It is somewhat remarkable that the ratios of constants for ethyl phenylmethoxyacetate and ethyl phenylethoxyacetate, and for ethyl phenylethoxyacetate and ethyl phenylpropoxyacetate, are very approximately 3 : 2 and 6 : 5. Whether this is merely a coincidence cannot yet be said. It must be remembered that the constant for the ethyl phenylpropoxyacetate has only been obtained indirectly.

On account of the ready saponifiability and the sparing solubility of some of the esters in water, measurements of the velocity of

saponification were also carried out in aqueous alcoholic solution. The results are given in the following table (see Tables 7—19):

	In 30 per cent. alcohol. *k*.	In 60 per cent. alcohol. *k*.
Ethyl phenylacetate	8·6	(6)
Methyl mandelate	(109)	(84)
Ethyl mandelate	49·4	29·1
Propyl mandelate	39·5	22·7
Ethyl phenylmethoxyacetate.....	15·2	(8)
Ethyl phenylethoxyacetate	10·2	(6)
Ethyl phenylpropoxyacetate	—	(5)

In 30 per cent. aqueous alcoholic solutions, fairly concordant values of the saponification constant could be obtained, except in the case of methyl mandelate; but in 60 per cent. alcoholic solutions there was a considerably greater falling off in the constant as the reaction proceeded, and the values of the constants given are therefore all more or less approximate. This applies also to some extent to the constants given for ethyl and propyl mandelates (Table 16), although, as the falling off in the value of the constants was not so great, we have ventured to take the mean.

Certain other irregularities also were met with in the case of the saponification in alcoholic solution, but as it is proposed by one of us to continue the investigation of the saponification velocities in alcoholic solution, the discussion of these may be left over until further data have been obtained.

Experimental.

Methyl Mandelate.—By the action of methyl iodide on silver mandelate, Naquet and Louguinine (*Annalen*, 1866, **139**, 299) obtained a product melting at 113—114°, whilst Breuer and Zincke (*Ber.*, 1880, **13**, 636), using the same method, obtained a product melting at 47—48°. This method was also employed by Rupe (*Ber.*, 1895, **28**, 259), who found the melting point to be 52°.

The process which we employed is based on the general method given by Fischer and Speier (*Ber.*, 1895, **28**, 3254). Twenty grams of mandelic acid were mixed with 60 grams of pure methyl alcohol and 6 grams of concentrated sulphuric acid, and the mixture heated on the water-bath for 5 hours. Most of the alcohol was then distilled off and the residue poured into water. The solution was neutralised with sodium carbonate, the ester extracted with ether, and the ethereal solution dried over sodium sulphate. After evaporating off the ether, the residue was distilled under 30 mm. pressure, when a colourless oil passed over at a temperature of 153° and quickly solidified in the receiver. The yield was 17·5 grams. After crystallising from ligroin alone and from a mixture of ligroin and benzene, the melting point

of the ester was found to be 57°;* it boiled at 250° with slight decomposition.

This method has also been used by Acree (*Ber.*, 1904, **37**, 2767), who gives the melting point as 58°.

0·1887 gave 0·1030 H_2O and 0·4503 CO_2. C = 65·1; H = 6·06.
0·1884 „ 0·1040 H_2O „ 0·4496 CO_2. C = 65·0; H = 6·13.
$C_9H_{10}O_3$ requires C = 65·06; H = 6·07 per cent.

Ethyl Mandelate.—In preparing this ester, we employed Fischer and Speier's method, which had previously been used by McKenzie (Trans., 1899, **75**, 755). The latter gives the melting point as 37°, but we failed, even by repeated crystallisation from ligroin and from ethyl acetate and ligroin, to raise the melting point higher than 29°.

0·1712 gave 0·1072 H_2O and 0·4187 CO_2. C = 66·7; H = 6·95.
$C_{10}H_{12}O_3$ requires C = 66·66; H = 6·66 per cent.

Propyl Mandelate.—Twenty grams of mandelic acid were mixed with 80 grams of propyl alcohol and 6 grams of concentrated sulphuric acid, and the mixture heated in an oil-bath at 110—115° for 7 hours. The product was then treated as in the preparation of methyl mandelate. A colourless oil was obtained which distilled at 145° under 12 mm. pressure, and solidified in needles on immersion in a freezing mixture. The ester melted at 14—15° and boiled, with partial decomposition, at 263°. The yield was 20 grams.

0·1976 gave 0·1328 H_2O and 0·4894 CO_2. C = 67·5; H = 7·47.
$C_{11}H_{14}O_3$ requires C = 68·04; H = 7·28 per cent.

Ethyl Phenylchloroacetate.—In order to obtain the alkoxyl derivatives of phenylacetic acid, it was first necessary to prepare ethyl phenylchloroacetate.

First method: Three hundred and fifty grams of ethyl mandelate were dissolved in a moderate volume of chloroform in a large flask, and 416 grams of phosphorus pentachloride added in small quantities from time to time. The mixture was then warmed on a water-bath at about 50° until no further action occurred. The excess of phosphorus pentachloride was destroyed by cautious addition of water, and the heavy oil which separated out was washed with water; it was then treated with sodium carbonate until slightly alkaline, and the ester then extracted with chloroform. The solution was dried over fused sodium sulphate and distilled under reduced pressure. Under 19 mm. pressure, a nearly

* When first prepared, the melting point was found to be 54°, but when this was again determined, after the lapse of about a year, the substance was found to melt at 57°.

colourless oil passed over at 142°. On analysis, it showed no trace of phosphorus.

0·2429 gave 0·1792 AgCl. Cl = 18·24.
0·2246 „ 0·1602 AgCl. Cl = 17·63.
$C_{10}H_{11}O_2Cl$ requires Cl = 17·85 per cent.

Second method: Fifteen grams of ethyl mandelate were treated with 42 grams of thionyl chloride, and the mixture was heated for 8 hours on the water-bath in a reflux apparatus. The excess of thionyl chloride was removed by warming on the water-bath, and the residue distilled under reduced pressure. A colourless oil was obtained which boiled at 143° under 25 mm. pressure, the yield being 14 grams.

0·2796 gave 0·2032 AgCl. Cl = 17·97 per cent.
0·3056 „ 0·2199 AgCl. Cl = 17·79 „

Preparation of the Alkoxyl Esters.

The methyl ester of phenylmethoxyacetic acid was prepared by Meyer and Boner (*Annalen*, 1883, **220**, 45) by acting on methyl phenylchloroacetate with sodium methoxide in methyl-alcoholic solution, and obtained as a pure product after two distillations. We endeavoured to utilise this method for the preparation of the alkoxyl derivatives of ethyl mandelate, but although quite a number of experiments were carried out with sodium methoxide, ethoxide, and propoxide, we found it a matter of the greatest difficulty, and in some cases we were unable to obtain alkoxyl esters quite free from chlorine. Even after thrice repeating the treatment with sodium ethoxide, a small quantity of the phenylchloroacetate appeared to have escaped decomposition. It was found impossible to effect a separation of the alkoxyl ester from the chloro-ester by fractional distillation under reduced pressure, although this could be done by fractionation under atmospheric pressure. The process, however, was very troublesome and was accompanied by loss of ester, so that the above method of preparation was abandoned.

It may be mentioned that exactly similar results were obtained with ethyl phenylchloroacetate prepared by the action of thionyl chloride as from specimens obtained by the action of phosphorus pentachloride, so that the difficulty experienced in getting rid of all the chloro-compound could not have been due to chlorination in the benzene ring.

Although we did not investigate the matter further, it may be stated that replacement of chlorine by the alkoxyl group took place with greater readiness in the case of sodium methoxide than in that of sodium ethoxide, and this, in turn, with greater ease than in the case of the propoxide. Since it is not at all improbable that the methyl

ester of phenylchloroacetic acid is more reactive than the ethyl ester, the success of the reaction in the preparation of methyl methoxymandelate by Meyer and Boner can be understood. We hope, however, to be able at a later date to undertake a quantitative study of the replacement of the chlorine by the alkoxyl group in the above reaction.

Ethyl Phenylmethoxyacetate.—The above method having proved unsuccessful, we decided to prepare first the free phenylmethoxyacetic acid and to esterify this. For the preparation of the acid, the method of Meyer and Boner was followed. The small amount of chloro-ester which escaped conversion was converted into sodium mandelate by the action of caustic soda, and could thus be separated by crystallisation from the sodium salt of phenylmethoxyacetate.

Phenylmethoxyacetic acid was isolated by decomposing the sodium salt with sulphuric acid, and when purified by crystallisation from benzene and ligroin melted at 69° (McKenzie, Trans., 1899, **75**, 760).

Nine grams of pure phenylmethoxyacetic acid were boiled for 6 hours with 30 grams of absolute ethyl alcohol and 2 grams of strong sulphuric acid. After distilling off the alcohol and neutralising the residue with potassium carbonate, the ester was extracted with ether, when 7·5 grams of a colourless oil were obtained, boiling at 141° under 26 mm. pressure.

0·2014 gave 0·1325 H_2O and 0·5027 CO_2. C = 68·06 ; H = 7·31.
$C_{11}H_{14}O_3$ requires C = 68·04 ; H = 7·28 per cent.

Ethyl Phenylethoxyacetate.—McKenzie (*loc. cit.*) has prepared ethyl *l*-phenylethoxyacetate by esterifying the free acid which he obtained by acting on *l*-mandelic acid with ethyl iodide and silver oxide. For the preparation of the inactive ester, the following method was employed. Thirty grams of ethyl phenylchloroacetate were boiled with 6 grams of sodium dissolved in 100 grams of ethyl alcohol for 12 hours. The resulting ethoxy-ester, which contained a slight admixture of the chloro-ester, was treated with caustic soda, whereby sodium phenylethoxyacetate was obtained as a mass of fine needles (compare Koerner and Radziszewski, *Zeit. Chemie*, 1868, **4**, 143), whilst the sodium mandelate formed from the chloro-ester present remained in solution. The sodium salt was then decomposed by means of sulphuric acid, and in this way phenylethoxyacetic acid was obtained as a viscid, pale yellow oil, which could not be made to crystallise. An analysis of the silver salt gave Ag = 37·39 per cent., whereas the theory requires 37·35.

The acid was then esterified in exactly the same manner as phenylmethoxyacetic acid. Ethyl phenylethoxyacetate was obtained as a

colourless oil, which boils at 134° under 13 mm. pressure and at 255° under atmospheric pressure.

0·2018 gave 0·5090 CO_2 and 0·1392 H_2O. C = 68·8; H = 7·66.
0·2092 ,, 0·5324 CO_2 ,, 0·1437 H_2O. C = 69·4; H = 7·63.
$C_{12}H_{16}O_3$ requires C = 69·23; H = 7·69 per cent.

Ethyl Phenylpropoxyacetate.—Thirty grams of ethyl phenylchloroacetate were boiled for four hours with 120 grams of propyl alcohol in which 8 grams of sodium had been dissolved. After removing the salt which separated, the liquid was again boiled for five hours with a further quantity of sodium propoxide. After treating the extracted esters with caustic soda and evaporating to dryness, sodium phenylpropoxyacetate was obtained. From this ester, phenylpropoxyacetic acid was obtained by hydrolysing with sulphuric acid, and as it is sparingly soluble was freed from any mandelic acid present by washing thoroughly with water. The acid was then taken up with ether and the ethereal solution dried over sodium sulphate. Phenylpropoxyacetic acid was thus obtained as a light yellow oil, the yield being 14—15 grams. Analyses of the silver salt gave Ag = 35·55 and 35·87 per cent., whilst theory requires Ag = 35·85.

The ethyl ester of phenylpropoxyacetic acid was then prepared in a manner similar to that used for the esterification of the phenylmethoxy- and phenylethoxy-acids. It was obtained as a colourless oil which distilled over at 144° under 13 mm. pressure.

0·2006 gave 0·5107 CO_2 and 0·1462 H_2O. C = 69·4; H = 8·1.
0·2104 ,, 0·5422 CO_2 ,, 0·1515 H_2O. C = 70·3; H = 8·0.
$C_{13}H_{18}O_3$ requires C = 70·2; H = 8·15 per cent.

Velocity of Saponification. A. In Aqueous Solution.

TABLE I.—*Ethyl Phenylacetate.*

N/150 ester; *N*/150 NaOH.

(*a*) *k* = 12·42 [extreme values, 11·69 and 12·99].
(*b*) *k* = 12·43 [,, ,, 11·96 ,, 12·84].
General mean: *k* = **12·42**.

TABLE II.—*Methyl Mandelate.*

First series:—*N*/30 ester; *N*/30 NaOH.

(*a*) *k* = 157·1 [extreme values, 151·9 and 164·7].
(*b*) *k* = 155·5 [,, ,, 152·8 ,, 161·2].

Second series:—*N*/60 ester; *N*/60 NaOH.

(*a*) *k* = 160·1 [extreme values, 153·8 and 165·9].
(*b*) *k* = 156·8 [,, ,, 150·4 ,, 160·9].
General mean: **157·4**.

TABLE III.—*Ethyl Mandelate.*

First series:—*N*/30 ester; *N*/30 NaOH.

(*a*) $k=65·1$ [extreme values, 60·6 and 68·1].
(*b*) $k=64·9$ [,, ,, 61·8 ,, 67·4].

Second series:—*N*/60 ester; *N*/60 NaOH.

(*a*) $k=66·9$ [extreme values, 63·7 and 69·9].
(*b*) $k=68·7$ [,, ,, 63·1 ,, 73·2].

General mean: $k=$ **66·4**.

TABLE IV.—*Propyl Mandelate.*

N/60 ester; *N*/60 NaOH.

(*a*) $k=55·6$ [extreme values, 51·1 and 58·0].
(*b*) $k=55·4$ [,, ,, 52·4 ,, 58·2].

General mean: **55·5**.

TABLE V.—*Ethyl Phenylmethoxyacetate.*

N/60 ester; *N*/60 NaOH.

(*a*) $k=23·4$ [extreme values, 22·7 and 24·0].
(*b*) $k=23·3$ [,, ,, 22·5 ,, 23·8].

General mean: **23·3**.

TABLE VI.—*Ethyl Phenylethoxyacetate.*

N/150 ester; *N*/150 NaOH.

(*a*) $k=15·6$ [extreme values, 14·8 and 17·1].
(*b*) $k=15·8$ [,, ,, 15·0 ,, 17·9].

General mean: **15·7**.

B. *Saponification in Aqueous-alcoholic Solution.*

I. *Solutions containing* 30 *per cent. of Alcohol.*

TABLE VII.—*Ethyl Phenylacetate.*

First series:—*N*/40 ester; *N*/30 NaOH.

(*a*) $k=8·62$ [extreme values, 8·24 and 9·10].
(*b*) $k=8·53$ [,, ,, 8·19 ,, 8·97].

Second series:—*N*/60 ester; *N*/60 NaOH.

(*a*) $k=8·67$ [extreme values, 8·43 and 9·02].
(*b*) $k=8·63$ [,, ,, 8·21 ,, 9·01].
(*c*) $k=8·60$ [,, ,, 8·41 ,, 8·75].

General mean: **8·61**.

TABLE VIII.—*Methyl Mandelate.*

$N/30$ ester; $N/30$ NaOH; T = titre in c.c. of $N/115 \cdot 1$ HCl.

Time.	T.	k.	Time.	T.	k.
0·0 mins.	19·26	—	0·0 mins.	19·26	—
1·22 ,,	6·04	108·6	1·22 ,,	6·04	109·0
2·30 ,,	3·84	106·3	2·22 ,,	4·01	104·7
3·72 ,,	2·75	98·9	3·72 ,,	2·79	97·9
5·22 ,,	2·18	92·6	5·22 ,,	2·22	91·8
7·22 ,,	1·72	87·8	7·22 ,,	1·76	86·3
9·22 ,,	1·48	83·4	9·22 ,,	1·51	80·2
12·22 ,,	1·26	73·7	12·22 ,,	1·26	74·7
17·22 ,,	0·98	69·3	17·22 ,,	0·99	69·7
24 hours	0·12	—	27·22 ,,	0·78	58·0
			24 hours	0·15	—

TABLE IX.—*Ethyl Mandelate.*

$N/30$ ester; $N/30$ NaOH.

(*a*) $k = 49 \cdot 5$ [extreme values, 47·6 and 51·1].
(*b*) $k = 48 \cdot 6$ [,, ,, 46·3 ,, 49·9].
(*c*) $k = 50 \cdot 0$ [,, ,, 47·3 ,, 51·9].

General mean: **49·4**.

TABLE X.—*Propyl Mandelate.*

$N/60$ ester; $N/60$ NaOH.

(*a*) $k = 39 \cdot 5$ [extreme values, 35·1 and 42·4].
(*b*) $k = 39 \cdot 5$ [,, ,, 36·4 ,, 41·9].

General mean: **39·5**.

TABLE XI.—*Ethyl Phenylmethoxyacetate.*

First series:—$N/40$ ester; $N/30$ NaOH.

(*a*) $k = 15 \cdot 0$ [extreme values, 14·3 and 15·5].
(*b*) $k = 15 \cdot 2$ [,, ,, 14·2 ,, 15·9].

Second series:—$N/60$ ester; $N/60$ NaOH.

(*a*) $k = 15 \cdot 2$ [extreme values, 14·5 and 15·8].
(*b*) $k = 15 \cdot 5$ [,, ,, 15·0 ,, 15·7].

General mean: **15·2**.

TABLE XII.—*Ethyl Phenylethoxyacetate.*

First series:—*N*/40 ester; *N*/30 NaOH.

(*a*) k=9·85 [extreme values, 9·41 and 10·34].
(*b*) k=9·95 [,, ,, 9·29 ,, 10·62].

Second series:—*N*/60 ester; *N*/60 NaOH.

(*a*) k=10·44 [extreme values, 9·95 and 10·93].
(*b*) k=10·41 [,, ,, 9·82 ,, 10·87].

General mean: 10·2.

II. *Solutions containing* 60 *per cent. of Alcohol.*

TABLE XIII.—*Ethyl Phenylacetate.*

N/70 ester; *N*/60 NaOH; *T*=titre in c.c. of *N*/117·0 HCl.

Time.	*T.*	*k.*	Time.	*T.*	*k.*
0·0 mins.	9·81	—	0·0 mins.	9·81	—
1·24 ,,	9·27	6·45	1·23 ,,	9·27	6·52
2·74 ,,	8·85	5·45	2·73 ,,	8 88	5·31
4·24 ,,	8·54	4·84	4·23 ,,	8·55	4·84
6·24 ,,	8·11	4·64	6·23 ,,	8·14	4·59
8·24 ,,	7·63	4·84	8·23 ,,	7·73	4·58
11·24 ,,	7·17	4·60	11·23 ,,	7·21	4·80
14·24 ,,	6·69	4·64	15·23 ,,	6 63	4·48
19·24 ,,	6·08	4·57	21·23 ,,	5·94	4·33
24·24 ,,	5·67	4·35	28·23 ,,	5·37	4·29
32·24 ,,	5·10	4·21	36·23 ,,	4·83	4·24
40·24 ,,	4·53	4·34	44·23 ,,	4·41	4·20
50·24 ,,	4·09	4·26	54·23 ,,	4·02	4·11
60·24 ,,	3·72	4·20	24 hours	1·28	—
24 hours	1·25	—			

TABLE XIV.—*Methyl Mandelate.*

N/70 ester; *N*/60 NaOH; *T*=titre in c.c. of *N*/115·8 HCl.

Time.	*T.*	*k.*	Time.	*T.*	*k.*
0·0 mins.	9·86	—	0·0 mins.	9·86	—
1·23 ,,	5·80	83·6	1·23 ,,	5·82	82·5
2·23 ,,	4·67	75·5	2·23 ,,	4·69	74·3
3·73 ,,	3·89	66·0	3·73 ,,	3·94	63·9
5·73 ,,	3·32	58·0	5·73 ,,	3·34	56·8
7·73 ,,	2·96	53·3	7·73 ,,	3·01	51·4
10·73 ,,	2·66	46 8	10·73 ,,	2·68	45·8
13·73 ,,	2·46	42·6	13·73 ,,	2·46	42·1
18·73 ,,	2·21	38·9	18·73 ,,	2·21	38·2
24 hours	1·46	—	24 hours	1·43	—

TABLE XV.—*Ethyl Mandelate.*

N/70 ester; *N*/60 NaOH.

(*a*) k=29·6 [extreme values, 27·5 and 31·4].
(*b*) k=28·6 [,, ,, 25·4 ,, 31·3].

General mean: 29·1.

TABLE XVI.—*Propyl Mandelate.*

N/70 ester; *N*/60 NaOH; *T* = titre in c.c. of *N*/114·8 HCl.

Time.	*T*.	*k*.	Time.	*T*.	*k*.
0·0 mins.	9·75	—	0·0 mins.	9·75	—
1·75 ,,	7·29	27·0	1·75 ,,	7·29	26·9
3·75 ,,	5·92	24·8	3·75 ,,	5·92	24·7
5·75 ,,	5·04	24·0	5·75 ,,	5·03	24·0
8·75 ,,	4·16	23·6	8·75 ,,	4·17	23·3
11·75 ,,	3·62	22·9	11·75 ,,	3·60	23·0
16·75 ,,	3·07	21·7	16·75 ,,	3·04	22·0
21·75 ,,	2·69	21·2	21·75 ,,	2·65	21·7
29·75 ,,	2·33	20·3	29·75 ,,	2·31	20·4
39·75 ,,	2·09	18·8	39·75 ,,	2·04	19·5
24 hours	1·33	—	24 hours	1·31	—
	Mean...........	22·7		Mean.....	22·8

General mean: 22·7.

TABLE XVII.—*Ethyl Phenylmethoxyacetate.*

N/70 ester; *N*/60 NaOH; *T* = titre in c.c. of *N*/117·0 HCl.

Time.	*T*.	*k*.	Time.	*T*.	*k*.
0·0 mins.	9·76	—	0·0 mins.	9·76	—
1·24 ,,	8·99	9·56	1·24 ,,	9·07	8·51
2·74 ,,	8·38	8·36	2·74 ,,	8·31	8·90
4·24 ,,	7·87	7·93	4·24 ,,	7·79	8·39
6·24 ,,	7·23	7·92	6·24 ,,	7·26	7·80
8·24 ,,	6·72	7·81	8·24 ,,	6·62	8·24
11·24 ,,	6·08	7·75	11·24 ,,	6·06	7·86
14·24 ,,	5·53	7·83	14·24 ,,	5·22	7·91
19·24 ,,	4·92	7·59	19·24 ,,	4·87	7·81
24·24 ,,	4·47	7·37	24·24 ,,	4·44	7·52
34·24 ,,	3·80	7·16	34·24 ,,	3·78	7·28
24 hours	1·25	—	24 hours	1·28	—

TABLE XVIII.—*Ethyl Phenylethoxyacetate.*

N/70 ester; *N*/60 NaOH; *T* = titre in c.c of *N*/116·5 HCl.

Time.	*T*.	*k*.	Time.	*T*.	*k*.
0·0 mins.	9·80	—	0·0 mins.	9·80	—
1·24 ,,	9·05	9·06	1·24 ,,	9·03	9·33
3·24 ,,	8·41	6·95	3·24 ,,	8·40	7·01
5·24 ,,	7·87	6·40	5·24 ,,	7·91	6·25
8·24 ,,	7·25	5·90	8·24 ,,	7·31	5·71
11·24 ,,	6·73	5·65	11·24 ,,	6·67	5·79
15·24 ,,	6·17	5·43	15·24 ,,	6·18	5·40
19·24 ,,	5·64	5·44	19·24 ,,	5·74	5·21
25·24 ,,	5·11	5·23	25·24 ,,	5·13	5·19
31·24 ,,	4·69	5·08	31·24 ,,	4·66	5·15
39·24 ,,	4·20	5·06	39·24 ,,	4·27	4·89
49·24 ,,	3·71	5·08	49·24 ,,	3·79	4·88
24 hours	1·16	—	24 hours	1·16	—

TABLE XIX.—*Ethyl Phenylpropoxyacetate.*

N/70 ester ; *N*/60 NaOH ; *T* = titre in c.c. of *N*/116·5 HCl.

Time.	*T*.	*k*.
0·0 mins.	9·82	—
1·24 ,,	9·28	6·41
3·24 ,,	8·76	5·12
9·24 ,,	7·47	4·74
17·24 ,,	6·39	4·51
24·24 ,,	5·67	4·34
38·24 ,,	4·72	4·18
56·24 ,,	3·91	4·13
24 hours	1·25	—

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LXXVII.—*Complex Nitrites of Bismuth.*

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THE author has been unable to find a description of any nitrites of bismuth, although such compounds evidently exist, for on adding powdered bismuth nitrate to a strong solution of an alkali nitrite an orange liquid is formed, and nitrous fumes are evolved. When a large amount of the bismuth salt has been added, the colour of the solution is deep orange, with a purplish reflex. This liquid rapidly absorbs oxygen from the air, its surface becoming covered with a white film of basic bismuth nitrate.

A similar solution may also be obtained by mixing the powdered salts with acetone; the resulting orange liquid, on evaporation in absence of air, leaves a yellow, crystalline mass. If potassium nitrite is used instead of the sodium salt, needle-shaped crystals are formed on evaporation, but in either case they rapidly decompose. Various attempts were made to isolate a more stable crystalline derivative from the orange solutions, but the only successful method was to pour the liquid, obtained by adding bismuth nitrate to saturated aqueous sodium nitrite into an aqueous solution of ammonium nitrate saturated at 0°. A yellow, crystalline, and very unstable substance is precipitated, which is described in the sequel.

a. *Bismuth Sodium Ammonium Nitrite.*

A more stable compound is obtained by dissolving powdered bismuth nitrate in a saturated solution of ammonium nitrate at 0°,

and then gradually pouring this liquid into an ice-cold, nearly saturated solution of sodium nitrite, slightly acidified with nitrous fumes. The best proportions are 10 grams of bismuth nitrate, 15 grams of ammonium nitrate, and 15 grams of sodium nitrite; but these numbers may be varied considerably.

The liquid must be at once poured off and the precipitate drained on a porous tile. It is then pressed several times between filter paper to remove adherent liquid, and the drying is completed by compressing the substance between pieces of porous plate in a desiccator kept at 0°. It is essential to dry the product in this manner, otherwise decomposition takes place.

Bismuth sodium ammonium nitrite, $Bi(NO_2)_3,2NH_4NO_2,NaNO_2$, is a bright yellow substance which crystallises in octahedra, and possesses a slight green fluorescence. It decomposes slowly at 0°, more rapidly at the ordinary temperature, evolving nitric oxide and leaving a moist white mass which contains no nitrite. If some of the substance is touched at any point with a hot wire, decomposition rapidly occurs throughout, and the resulting white mass is found to be free from nitrite. The substance detonates feebly on being struck.

ANALYSIS.

Found.

Preparation.	Bi.	Na.	NH_4.	NO_2 per cent.
(1)	38·9 ; 39·1	4·54	6·30	49·7
(2)	39·5	4·48	6·25	49·8

Calculated.

	Bi.	Na.	NH_4.	NO_2 per cent.
	38·25	4·24	6·64	50·87

The methods of analysis are described later (p. 765). The slight deficits in the ammonium and nitrite are probably due to interaction between these constituents.

b. *Bismuth Potassium Nitrite.*

The most stable of these compounds is obtained by passing nitrous fumes into a suspension of bismuth hydroxide in concentrated potassium nitrite solution until white particles can no longer be seen in the orange precipitate. The product should be dried quickly, as when moist it absorbs oxygen.

Bismuth potassium nitrite, $Bi(NO_2)_3,3KNO_2,H_2O$, is an orange, crystalline, and slightly fluorescent substance. Like the other compounds described, it is immediately hydrolysed by water; but,

unlike them, it is stable at the ordinary temperature, and does not detonate when struck.

ANALYSIS.

Found.

Preparation.	Bi.	K.	NO_2.	Water by difference per cent.
(1)	34·1	19·09	44·3	2·5
(2)	33·8	19·06	44·2	2·8
(3)	—	—	44·6	—

Calculated.

	Bi.	K.	NO_2.	Water
	33·5	18·96	44·6	2·9

The formulæ of these two compounds resemble those of many complex nitrites of other elements in having an atom of the monad metal for each valency of the polyvalent metal, as, for instance, $Co(NO_2)_3,3NaNO_2,H_2O$ and $Co(NO_2)_2,2KNO_2,H_2O$.

c. *Other Complex Bismuth Nitrites.*

The compound obtained by mixing bismuth nitrate with sodium nitrite and adding the mixture to ammonium nitrate (p. 761) is both more complex and less stable than those already described. It may be obtained by mixing 15 or 20 grams of powdered bismuth nitrate with a saturated aqueous solution of 15 grams of sodium nitrite. The resulting orange liquid is then filtered, preferably in absence of air, although instead of excluding air it is sufficient to filter the liquid quickly by suction. As soon as the filtrate becomes clear, it is allowed to drop slowly into saturated ammonium nitrate solution, kept at 0°. The supernatant liquid is rapidly poured off, and the yellow precipitate carefully dried, first with filter paper and then in a desiccator at 0° (p. 762); it is advantageous to replace the air in the desiccator by nitrogen.

The *substance* thus obtained, which is most probably

$$Bi(NO_2)_3,2NH_4NO_2,NH_4NO_3,NaNO_3,$$

forms small, canary-yellow crystals, possessing a green fluorescence; it gradually decomposes, even at 0°, becoming white and evolving nitric oxide. If the salt is kept in a bottle, the decomposition is rapid, and the residue becomes moist, owing to the water produced from the ammonium nitrite, but in a desiccator the decomposition is slower, because of the removal of the water as it is formed. The decomposition is complex, as in addition to the resolution of the ammonium nitrite into nitrogen and water, and the liberation of nitric oxide from the bismuth nitrite, there is further a gradual absorption of oxygen.

The substance detonates feebly when struck, and is decomposed throughout when touched by a hot wire. It thus resembles bismuth sodium ammonium nitrite, from which it may be regarded as being derived by the replacement of a molecule of ammonium nitrite by ammonium nitrate and the addition of a molecule of sodium nitrate.

On account of the unusual character of the foregoing formula numerous analyses were made on specimens prepared under various conditions. The proportion of bismuth nitrate to sodium nitrite was varied between 3:5 and 5:3 by weight, and the ammonium nitrate was, in some cases, added to the mixture of bismuth nitrate and sodium nitrite; but the analyses showed no parallel variations. When the substance was precipitated fractionally, the variations were also small and irregular, and this renders it unlikely that the substance could be a mixture of two or more salts precipitated together; the composition of a precipitate would in such case change as the concentration of the dissolved salts altered.

Analysis.

Found (mean).

	Bi.	Na.	NH_4.	NO_2.	NO_3 per cent.
	32·6	3·59	8·32	34·3	19·0
Number of determinations of each constituent.........	(5)	(5)	(8)	(15)	(5)

Calculated.

	Bi.	Na.	NH_4.	NO_2.	NO_3 per cent.
	32·5	3·60	8·46	36·0	19·4

The numbers are fairly concordant except for the nitrite; the bismuth and sodium showed a very constant ratio. The ammonium and nitrite are low, probably in part on account of some action between them. The bismuth is not present as a basic salt, for the acids are equivalent to the bases; in this the compound differs from the nitrate-nitrites of lead, which are all basic.

The tendency of these compound bismuth nitrites to oxidise is not entirely due to hydrolysis into bismuth hydroxide and nitrous acid, followed by decomposition of the latter. The orange liquid, obtained by mixing bismuth nitrate and sodium nitrite, became coated with a white film immediately it came into contact with the air, and direct measurement proved that such a solution absorbed oxygen much more quickly than it evolved nitric oxide.

In addition to the above compounds, some other salts were prepared: an orange tetramethylammonium salt; a black triple nitrite of bismuth, copper, and ammonium; and a yellow com-

pound, apparently a double nitrite of bismuth and cinchonine. A light yellow solution is obtained by passing nitrous fumes into water containing bismuth hydroxide in suspension, and also by adding the hydroxide and a little water to the blue liquid obtained by condensing nitrous fumes. These solutions probably contain bismuth nitrite, but it was not found possible to prepare this substance in the solid state.

The slight fluorescence possessed by these salts suggested that they might be susceptible to radium, or to the cathode rays; but in neither case was any perceptible effect produced.

Methods of Analysis.

The bismuth was estimated as oxide or sulphide, and the sodium and potassium as sulphates. To estimate the ammonium, about 0·5 gram of the solution was weighed in a small tube, which was then dropped into cold caustic soda solution, the ammonia being then distilled into $N/10$ acid. If the substance is first added to water there is a slight loss of ammonia.

As the substance was decomposed immediately by water with evolution of nitrous fumes, and ammonium was present, it was found impossible to obtain concordant values for the nitrite, except by the following method. About 0·1 gram of the substance was weighed in a small tube; this was dropped into a 500 c.c. bottle, almost full of ice-cold acidified water, to which about one and a half times the calculated quantity of $N/10$ permanganate had been added. After a few minutes the excess of permanganate was estimated by ferrous sulphate. Control analyses were made on pure sodium nitrite and mixtures of sodium nitrite, ammonium nitrate, and bismuth nitrate; the method gave good results, whilst departures from this mode of procedure gave high and discordant values.

The nitrate was determined by difference, the total nitrogen in about 0·2 gram of the substance being converted into ammonia by reduction with aluminium and sodium hydroxide. Simultaneous determinations of the ammonium and nitrite were made on the same specimen, so that the nitrogen present as NO_3 was given by the difference. Three treatments with aluminium were usually necessary before all the nitrate and nitrite were reduced.

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LXXVIII.—*The Ultra-violet Absorption Spectra of Certain Enol-keto-tautomerides. Part II.*

By Edward Charles Cyril Baly and Cecil Henry Desch.

In the first part of this investigation (Trans., 1904, **85**, 1029) the ultra-violet absorption spectra of acetylacetone and ethyl acetoacetate and of certain derivatives of these compounds were described. Reasons were brought forward in support of the view that the absorption band obtained in photographing the ultra-violet spectrum of iron through solutions of these substances, according to Hartley's method, is due to the equilibrium existing between the two possible tautomeric forms. It was found that neither of the modifications, when in a pure state, gives an absorption band, but that when the two are present in equilibrium with one another, a very decided absorption band is developed. It was further pointed out that the persistence of this absorption band over a definite change of concentration may doubtless be taken as a measure of the relative number of molecules in the changing state. Finally, it was found that the oscillation frequency of the light waves absorbed is nearly the same in all the substances examined, whether these contained a hydrogen, glucinum, sodium, or even a thorium atom in the so-called labile condition. We therefore concluded that the absorption band cannot in any way be regarded as being directly due to an oscillating atom, that is to say, the vibration frequency of the atom cannot be the same as the oscillation frequency of the light absorbed. We have now investigated the ultra-violet absorption spectra of the following analogous substances: ethyl acetylsuccinate, ethyl diacetylsuccinate, ethyl benzoylacetate, ethyl oxaloacetate, ethyl acetonedicarboxylate, ethyl benzoylsuccinate, and benzoylacetone, together with certain of their metallic derivatives. The conclusions drawn in the previous paper have been fully confirmed; on the one hand, neither the pure hydroxylic nor the pure ketonic substance shows an absorption band, and on the other hand, the vibration-frequency of the absorption band seems to bear little relation to the mass of the atom in the labile state.

Only three of the substances dealt with in the present paper exhibit absorption bands in the free state, namely, benzoylacetone, ethyl benzoylacetate, and ethyl benzoylsuccinate. It is evident, therefore, that there must be in these three cases a considerable number of molecules in the oscillating state, whilst in the case of the remaining substances dealt with, almost all the molecules are probably quiescent; it is not possible to say with any certainty

whether the latter substances are enolic or ketonic, but it is probable, from a comparison of their absorption curves with those of acetonylacetone and ethyl ethoxyfumarate, that they are chiefly enolic.

The conclusion that the pure substances do not show any absorption band in their spectra is based on the results obtained with acetonylacetone, ethyl ethoxyfumarate, and hydroxymethylenecamphor. The details of the absorption spectra are given below, and it will be seen that there is no semblance of an absorption band developed in any of these substances. In acetonylacetone we have a purely ketonic compound, in ethyl ethoxyfumarate a derivative of the purely hydroxylic form of ethyl oxaloacetate, and in hydroxymethylenecamphor we have an analogous condition in the hydroxymethylene group. It may be pointed out that solutions of camphor itself of the strength we work with have been shown by Hartley to be quite diactinic, so that we are justified in attributing the absorption given by this substance entirely to the presence of the hydroxymethylene group.

With the exception of the aluminium derivatives of ethyl benzoylacetate and benzoylacetone, we have only been able to investigate the free compounds and their sodium derivatives; but, as can readily be seen from the experimental results given below, although the absorption bands are usually shifted towards the red in the metallic derivatives, the amount of shift is by no means the same in all the substances, and bears no simple relation to the masses of the metallic and hydrogen atoms. The slight shifting observed is only what would be expected from the small increase in the total mass of the molecule, as has so many times been pointed out by Hartley.

In attempting to find an explanation of the origin of the absorption band it is necessary to take a different view of the physical process from that usually held. It is perfectly evident that some vibration or free period must exist connected with the transition from one tautomeride to the other, which is synchronous with the oscillation frequency of the light rays absorbed. There seems to be no question of doubt that this vibration cannot be the vibration of the labile atom itself, for, apart from the fact that the oscillation-frequency of the absorption band bears little relation to the mass of this labile atom, it is also noteworthy that the oscillation-frequency of the band is far greater than that usually attributed to atomic motions. We are therefore driven to the conclusion that the absorption of light is due to the change of linking expressed by the following reversible equation:

$$-CH_2 \cdot CO- \quad \rightleftarrows \quad -CH:C(OH)-,$$

and not merely to the wandering of the labile atom. This may be expressed in another way by saying that the phenomenon is due to the change of condition of the two carbon atoms and the oxygen atom. If we consider in detail the transition from, for example, the enolic to the ketonic form, it will be seen that the hydrogen or other labile atom leaves the oxygen and wanders to the carbon atom; there must, however, obtain for an exceedingly short time a condition in which the hydrogen atom is half-way on its journey, when we cannot consider it to be definitely linked either to the oxygen or to the carbon atom. We may thus conceive the momentary existence of an intermediate transition phase, which can be expressed thus:

$$\begin{array}{c}-\mathrm{CH}\cdot\underset{|}{\mathrm{C}}-\\ \mathrm{H}\ \ \mathrm{O}\end{array}$$

During the existence of this transition phase the two carbon atoms and the oxygen atom are actually changing their linking. It seems probable that the absorption band is due to this change of linking, or, in other words, it is due to the above transition phase. It must not be forgotten that the oscillation-frequency of the absorption band appears to be too great to be connected in any way with the motions of the atoms *quâ* atoms, and therefore we are not able to attribute it to possible motions of the carbon or oxygen atoms.

In attempting to form a theory to account for the connection between the change of linking and the absorption of light, it is necessary to take account of certain facts which have been established experimentally by Hartley and others in this field. Firstly, no organic substance shows an absorption band unless a possibility of tautomerism exists in the molecule. Secondly, this tautomerism need not be due to a labile atom, but may be of the same order as that occurring in those aromatic substances containing the true benzenoid structure. Thirdly, in all cases of the simpler tautomeric molecules, the vibration-frequencies of the absorption bands are very nearly the same. Fourthly, an increase in the mass of the molecule causes a decrease in the oscillation-frequency of the absorption band.

Finally, we have Hewitt's theory of fluorescence, namely, that this phenomenon is due to a process of tautomerism. If this is accepted, it appears that a tautomeric substance is not only able to give rise to a selective absorption of light, but also in certain circumstances to act as a source of light.

Up to the present no theory has been brought forward to account for any of these facts, but it is possible to co-ordinate all of them,

and at the same time to explain the formation of the absorption bands by the same theory as that employed by physicists to explain the phenomena of radioactivity, emission spectra, series of spectral lines, the Zeeman effect, &c., namely, the electron theory. This theory postulates that each atom is a system of small particles or electrons, which are in continual motion round a common centre of gravity, and that the emission spectra of gases are due to vibrational disturbances of these systems of electrons. The combination between two atoms is accompanied by the passage of one or more electrons from one atom to the other, producing one or more Faraday tubes of force between them, each Faraday tube representing the chemist's single bond. If, by some means, we cause a rearrangement of these linkings or Faraday tubes, it is clear that there must occur a vibrational disturbance in the system of electrons. In all cases of tautomerism, the rearrangement of the linkings is the essence of the process, and therefore we should expect to find vibrational disturbances in the electrons of the atoms concerned. Now, we have direct evidence of these disturbances in the fluorescence of tautomeric substances, as shown by Hewitt. It is therefore only natural that the converse takes place, namely, the absorption of light by tautomeric substances. In the substances dealt with by us, at least three atoms in each molecule are undergoing change of linking, and therefore each one of these, owing to the resulting disturbance of the electrons, helps in the formation of the absorption band.

This theory of the formation of the absorption bands accompanying tautomerism is capable of bringing into line the facts observed in the ultra-violet absorption spectra, which were mentioned above. Firstly, the fact that the oscillation-frequencies of the absorption bands given by simple tautomeric substances are always very nearly the same—the changes of linking taking place are all of the same type, whether in the aromatic compounds containing the benzenoid nucleus or in the aliphatic tautomerides, and therefore the same type of vibrational disturbance on the electrons is set up, resulting in approximately the same frequency in the absorption band. Secondly, an increase in the mass of the molecule causes the oscillation-frequency of the band to decrease, and the band is shifted towards the red; the period of the vibrational disturbance of the electrons depends on the mass of matter in their immediate neighbourhood, and becomes slower when this mass is increased. This decrease in the period of the vibrations of the electrons, with increase in the mass of the molecule, is well shown by the spectral series of the several elements of the same family. This can be

seen at once from the following equations for the first members of the principal series of the alkali metals, where n is the oscillation-frequency, and m the number of the line in the series (=3, 4, 5, &c.).

Lithium	$n = 43584{\cdot}75 - \frac{133669}{m^2} - \frac{1100084}{m^4}$
Sodium..............	$n = 41542{\cdot}51 - \frac{130233}{m^2} - \frac{800791}{m^4}$
Potassium	$n = 35086{\cdot}55 - \frac{126983}{m^2} - \frac{625318}{m^4}$
Rubidium...........	$n = 33762{\cdot}11 - \frac{125531}{m^2} - \frac{562255}{m^4}$
Cæsium..............	$n = 31509{\cdot}31 - \frac{125395}{m^2} - \frac{486773}{m^4}$

These equations of Kayser and Runge show at once how the series is in each case bodily shifted towards the red with increasing mass. We have in this a very striking analogy between emission and absorption spectra.

The chemical aspect of tautomerism, as seen in the light of ultra-violet absorption spectra, is also very interesting. For example, solutions of the sodium and aluminium derivatives of ethyl aceto-acetate are equilibrium mixtures of the enolic and ketonic modifications, that is to say, the sodium and aluminium atoms respectively are oscillating between the two positions. Now, in the case of the sodium compound, there is distinct evidence of ionisation and hydrolysis, but in the case of the aluminium compound the ionisation and hydrolysis are very small. Now, Hartley (Trans., 1902, **81**, 571; 1903, **83**, 221) showed that metallic nitrates and nitric acid in solution give absorption bands, the position of which depends on the mass of the metal. These bands, however, are only developed in solutions which, according to the electrolytic dissociation hypothesis, are ionised, and Hartley, in this way, showed that there must be intimate connection between the metallic atom and the NO_3 group, even in dilute solutions, when the salts are more or less completely ionised. Even without this discovery of Hartley's, it is impossible to conceive of the bond of chemical attraction, or the Faraday tube between the two ions of a metallic salt, as being destroyed by simple solution. It would seem preferable to consider the action of the solvent as merely tending to draw the two ions apart. When the two ions are sufficiently separated to allow of an interchange of ions between different molecules, we then have the condition called ionisation. In this way, we do not picture the bands of affinity as being destroyed, but merely broken in one place and regenerated in another. It is possible, on these lines, to consider the whole phenomena of electrolytic dissociation from a far broader standpoint. When a compound is dissolved, the

tendency of the solvent is to separate the molecules into two or more ions. When the ions become sufficiently far removed from one another to permit of the interchange of ions between adjacent molecules, we have the condition of ionisation, which is partial, or more or less complete, according as to whether the interchanges are small or great in number per unit time. When, however, the separation of the ions has not reached the critical length, no interchange takes place, and we have the non-ionised condition, for example, mercuric cyanide in water. In this class we might include the many organic compounds which apparently react by ions, even although their solutions show little or no evidence of ionisation (compare Kahlenberg, *J. Physical Chem.*, 1902, **6**, 1). One class more may be included, namely, the aliphatic tautomeric substances, which may be regarded as being only sufficiently dissociated in solution to allow of interchanges between different parts of the same molecule. The labile atom is in a state of incipient dissociation, and may thus be looked upon as a potential ion.

The whole question of dissociation thus appears to be one merely of degree and not of kind, and there is no need to consider any discontinuity in the action of the solvent.

It is possible to put this view to the test in the case of the aliphatic tautomeric substances. We have already suggested that the persistence of the band is a measure of the number of molecules which are in the transitional state between the two forms; on the above view, this persistence is a measure of the extent to which the labile atoms are separated from the rest of the molecule.

There should exist, therefore, for every tautomeric substance, a maximum value of this persistence which corresponds to the condition that the separation of all the labile atoms from the rest of the molecule has overstepped the critical value, and that perfectly free interchanges are taking place. Now, we have shown that the addition of sodium hydroxide increases the persistence of the absorption band; successive additions of the alkali should therefore increase the persistence until the maximum value is reached, and the amount of hydroxide necessary to produce this should be far beyond that required to convert the whole of the substance into the sodium derivative. This is well evidenced by the addition of sodium hydroxide to the aluminium derivative of ethyl benzoylacetate, a large excess being necessary to produce the maximum persistence (compare Fig. 1). We have investigated the action of sodium hydroxide on ethyl benzoylsuccinate and have observed the absorption spectra of the substance in the free state and in the presence of one, ten, twenty, and one hundred equivalents of alkali.

The measurements of the persistence of the absorption band in each case are as follows:

	Free ester.	With 1 eq. of alkali.	With 10 eq. of alkali.	With 20 eq. of alkali.	With 100 eq. of alkali.
Absorption band begins at	120 mm.	63 mm.	40 mm.	31·7 mm.	21·9 mm.
Absorption band ends at	83·2 ,,	34·7 ,,	20 ,,	15·2 ,,	10·4 ,,
Change of dilution over which absorption band persists	30·7 %	44·9 %	50 %	52 %	52·5 %

The thicknesses given refer to a $N/10,000$ solution of the ester.

These results leave little doubt that the persistence of the absorption band is steadily increased by the addition of alkali until a maximum is reached; in the case of ethyl benzoylsuccinate, the maximum is apparently reached by the addition of 20 equivalents of sodium hydroxide, as an increase in the alkali to 100 equivalents only increases the persistence by 0·5 per cent.

EXPERIMENTAL.

Benzoylacetone.

This substance was obtained from Kahlbaum, and another specimen was prepared for us by Messrs. A. C. Carter and D. B. Byles. Both specimens were found to be pure after recrystallisation from alcohol. Solutions were made in absolute alcohol, and their absorption spectra photographed. The following measurements of the absorption band were obtained:

0·162 gram (1 milligram-molecule) in 1000 c.c.

Thickness of layer of solution in millimetres.	Description of spectrum.	$1/\lambda$.	λ.
60	Spectrum transmitted to	2810	3557
40	,, ,, ...	2815	3552
30	,, ,, ...	2820	—
20	,, ,, ...	2830	3532
10	,, ,, ...	2860	3496
9	,, ,, ...	2865	3490
8	,, ,, ...	2875	3477
	Absorption band...............	**2875—3800**	**3477—2630**
	Spectrum transmitted (weak)......	3800—3850	2630—2597
	Complete absorption beyond.		
6	Spectrum transmitted to	2900	3447
	Absorption band..................	**2900—3748**	**3447—2667**
	Spectrum transmitted	3748—3875	2667—2580
	Complete absorption beyond.		
4	Spectrum transmitted to	2935	3405
	Absorption band..................	**2935—3640**	**3405—2746**
	Spectrum transmitted	3640—4140	2746—2415

0·162 gram in 10,000 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	1/λ.	λ.
30	Spectrum transmitted to	2970	3366
	Absorption band..................	**2970—3558**	**3366—2810**
	Spectrum transmitted	3558—4290	2810—2330
	Complete absorption beyond.		
25	Spectrum transmitted to	3030	3299
	Absorption band..................	**3030—3480**	**3299—2873**
	Spectrum transmitted	3480—4320	2873—2314
	Complete absorption beyond.		
20	Spectrum transmitted to	3200	3124
	Absorption band..................	**3200—3300**	**3124—3029**
	Spectrum transmitted	3300—4340	3029—2303
	Complete absorption beyond.		
10	Spectrum transmitted to	4390	2277

Benzoylacetone in presence of Sodium Hydroxide.

0·162 gram in 1000 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	1/λ.	λ.
8	Spectrum transmitted to	2805	3565
6	,, ,, ...	2810	3558
	Absorption band..................	**2810—3500**	**3558—2857**
	Spectrum transmitted	3500—3900	2857—2562
	Complete absorption beyond.		
4	Spectrum transmitted to	2835	3526
	Absorption band..................	**2835—3400**	**3526—2938**
	Spectrum transmitted	3400—3860	2938—2589

0·162 gram in 10,000 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	1/λ.	λ.
30	Spectrum transmitted to	2890	3459
	Absorption band..................	**2890—3305**	**3459—3024**
	Spectrum transmitted	3305—4030	3024—2480
20	,, ,, to	2970	3366
	Absorption band..................	**2970—3220**	**3366—3104**
	Spectrum transmitted	3220—4190	3104—2384
15	,, ,, to	3020	3309
	Absorption band..................	**3020—3140**	**3309—3184**
	Spectrum transmitted	3140—4247	3184—2354
10	,, ,, to	4310	2319
8	,, ,, to	4360	2293
6	,, ,, to	4460	2241

Benzoylacetone, Aluminium Derivative.

The *aluminium* derivative of benzoylacetone, $Al(C_{10}H_9O_2)_3$, is readily prepared by adding an alcoholic solution of benzoylacetone (3 mols.) to a solution of aluminium chloride (1 mol.) and sodium acetate (3 mols.) in water. The aluminium derivative separates

immediately as a crystalline precipitate. It dissolves very sparingly in organic solvents, but may be recrystallised from a large volume of hot alcohol. It melts at 217°, but after being allowed to solidify again melts at 162°.

0·170 gram (1 milligram-equivalent) in 1000 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
8	Spectrum transmitted to	2800	3570
6	,, ,, ...	2805	3565
	Absorption band	**2805—3630**	**3565—2755**
	Spectrum transmitted	3630—3750	2755—2666
4	,, ,, to	2810	3557
	Absorption band	**2810—3560**	**3557—2809**
	Spectrum transmitted	3560—3800	2809—2631

0·170 gram in 10,000 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	2830	3532
	Absorption band	**2830—3480**	**3532—2873**
	Spectrum transmitted	3480—3870	2873—2583
25	,, ,, to	2855	3501
	Absorption band	**2855—3445**	**3501—2902**
	Spectrum transmitted	3445—3980	2902—2511
20	,, ,, to	2905	3441
	Absorption band	**2905—3400**	**3441—2938**
	Spectrum transmitted	3400—4155	2938—2406
10	,, ,, to	3000	3333
	Absorption band	**3000—3230**	**3333—3094**
	Spectrum transmitted	3230—4270	3094—2341
9	,, ,, to	3040	3288
	Absorption band	**3040—3190**	**3288—3133**
	Spectrum transmitted	3190—4350	3133—2298
8	Spectrum weak	3080—3120	3246—3204
	Spectrum transmitted to	4420	2262

Ethyl Benzoylacetate, $COPh\cdot CH_2\cdot CO_2Et$.

The free ester was obtained from Kahlbaum and was perfectly colourless. The aluminium derivative, $Al(C_{11}H_{11}O_3)_3$, was prepared by mixing an alcoholic solution of the ester (3 mols.) with an aqueous solution of aluminium chloride (1 mol.) and sodium acetate (3 mols.), alcohol being added to dissolve any precipitate which may be formed. The aluminium derivative separates after a time as a viscous oil, which slowly solidifies, and may be recrystallised from hot alcohol, in which it is rather sparingly soluble; it melts sharply at 135°. The absorption curves of these substances are shown in Fig. 1, in which curve 1 is that of the free ester, curve 2

is that of the aluminium derivative, curve 3 that of the ester in the presence of sodium hydroxide, and curve 4 that of the aluminium derivative in presence of sodium hydroxide.

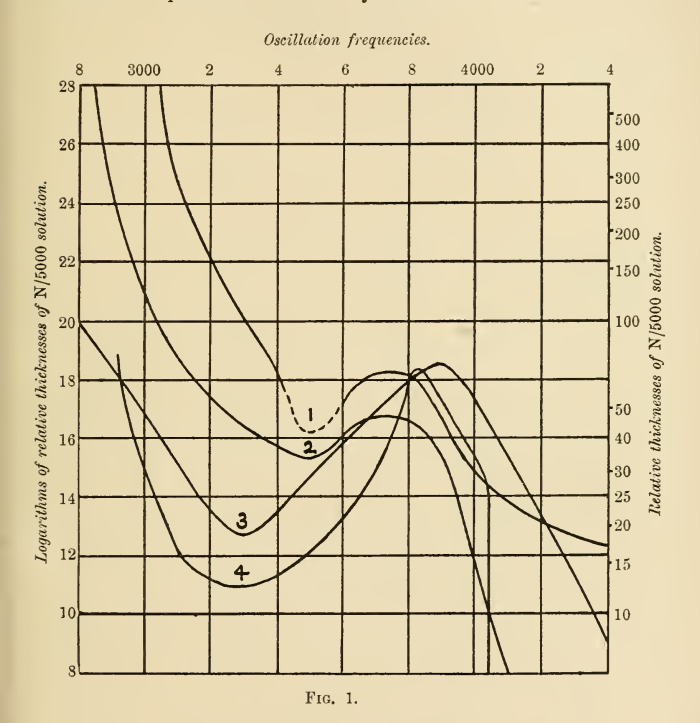


FIG. 1.

Ethyl Acetonedicarboxylate.

The substance, which was obtained from Kahlbaum, was quite colourless; it was twice redistilled and boiled at 167° under 45 mm. pressure.

The Ester in presence of Alkali Hydroxide.

0·202 gram (1 milligram-molecule) in 100 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3220	3105
20	,, ,, ...	3250	3076
10	,, ,, ...	3280	3048
8	,, ,, ...	3295	3034
6	,, ,, ...	3305	3025
4	,, ,, ...	3335	2997

0·202 gram in 1000 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3353	2982
20	,, ,, ...	3370	2966
10	,, ,, ...	3400	2940
8	,, ,, ...	3418	2925
7	,, ,, ...	3425	2919
	Absorption band.................	**3425—4040**	**2919—2474**
	Spectrum transmitted	4040—4220	2474—2369
6	,, ,, to	3437	2908
	Absorption band.................	**3437—3980**	**2908—2512**
	Spectrum transmitted	3980—4290	2512—2330
4	,, ,, to	3473	2879
	Absorption band.................	**3473—3880**	**2879—2577**
	Spectrum transmitted	3880—4410	2577—2267
3	,, ,, to	3520	2840
	Absorption band.................	**3520—3800**	**2840—2631**
	Spectrum transmitted	3800—4415	2631—2265
2·5	,, ,, to	3565	2804
	Absorption band.................	**3565—3750**	**2804—2666**
	Spectrum transmitted	3750—4417	2666—2263
2	Spectrum weak	3600—3700	2777—2702
	Spectrum transmitted to	4420	2262

Ethyl Acetonedicarboxylate.

0·202 gram (1 milligram-molecule) in 100 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3557	2810
20	,, ,, ...	3600	2776
10	,, ,, ...	3660	2731
8	,, ,, ...	3668	2716
6	,, ,, ...	3685	2712
4	,, ,, ...	3725	2684

0·202 gram in 1000 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3765	2655
20	,, ,, ...	3835	2607
10	,, ,, ...	4040	2474
8	,, ,, ...	4140	2415
6	,, ,, ...	4200	2380
5	,, ,, ...	4280	2336
4	,, ,, ...	4390	2277

Ethyl Oxaloacetate.

The sample employed was obtained from Kahlbaum; it was colourless, and when redistilled under 27 mm. pressure boiled at 132—133°.

0·188 gram (1 milligram-molecule) in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3225	3100
20	,, ,, ...	3270	3057
10	,, ,, ...	3345	2988
8	,, ,, ...	3360	2976
6	,, ,, ...	3365	2971
4	,, ,, ...	3390	2950

0·188 gram in 1000 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3405	2934
20	,, ,, ...	3420	2923
15	,, ,, ...	3470	2881
10	,, ,, ...	3560	2808
8	,, ,, ...	3730	2680
6	,, ,, ...	4005	2496
5	,, ,, ...	4200	2380
4	,, ,, ...	4365	2290

Ethyl Oxaloacetate in Alkaline Solution.

0·188 gram in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	2830	3352
20	,, ,, ...	2875	3477
10	,, ,, ...	2955	3383
	Absorption band..................	**2955—4050**	**3383—2468**
	Spectrum transmitted	4050—4170	2468—2397
8	,, ,, to	2980	3355
	Absorption band..................	**2980—3960**	**3355—2524**
	Spectrum transmitted	3960—4245	2524—2355
6	,, ,, to	3010	3321
	Absorption band........	**3010—3860**	**3321—2590**
	Spectrum transmitted	3860—4310	2590—2319
4	,, ,, to	3070	3256
	Absorption band............. ...	**3070—3720**	**3256—2687**
	Spectrum transmitted	3720—4400	2687—2272
3	,, ,, to	3130	3194
	Absorption band..................	**3130—3610**	**3194—2769**
	Spectrum transmitted	3610—4460	2769—2241
2·5	,, ,, to	3210	3114
	Absorption band.....	**3210—3515**	**3114—2844**
	Spectrum transmitted	3515—4510	2844—2217
2	Spectrum weak	3300—3420	3030—2923
	Spectrum transmitted to	4540	2202

Ethyl Ethoxyfumarate, $CO_2Et{\cdot}C(OEt){:}CH{\cdot}CO_2Et$.

This substance was very kindly supplied to us by Dr. Lander, and its absorption spectrum is of especial interest, as the compound may be regarded as a derivative of the enolic form of ethyl oxaloacetate. The specimen boiled at 135—137° under 11 mm. pressure.

0·216 gram (1 milligram-molecule) in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3260	3067
20	,, ,, ...	3290	3039
10	,, ,, ...	3350	2984
8	,, ,, ...	3360	2975
6	,, ,, ...	3370	2966
4	,, ,, ...	3400	2940

0·216 gram in 1000 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3433	2912
20	,, ,, ...	3500	2856
15	,, ,, ...	3550	2816
10	,, ,, ...	3645	2742
8	,, ,, ...	3680	2717
6	,, ,, ...	3720	2687
4	,, ,, ...	3840	2604

0·216 gram in 10,000 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3900	2563
20	,, ,, ...	4030	2481
10	,, ,, ...	4190	2386
8	,, ,, ...	4235	2361
6	,, ,, ...	4270	2341
4	,, ,, ...	4355	2296

Ethyl Acetylsuccinate, $CO_2Et{\cdot}CHAc{\cdot}CH_2{\cdot}CO_2Et$.

This substance was obtained from Kahlbaum and on being distilled boiled at a constant temperature.

Free Ester.

0·216 gram (1 milligram-molecule) in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3550	2816
20	,, ,, ...	3640	2746
10	,, ,, ...	3740	2673
8	,, ,, ...	3825	2614
6	,, ,, ...	3940	2537
5	,, ,, ...	4000	2499
4	,, ,, ...	4030	2481
2	,, ,, ...	4040	2474

0·216 gram in 1000 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
15	Spectrum transmitted to	4220	2369
10	,, ,, ...	4400	2272

Ethyl Acetylsuccinate in presence of Alkali Hydroxide.

0·216 gram in 100 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3140	3183
20	,, ,, ...	3170	3153
10	,, ,, ...	3220	3105
8	,, ,, ...	3240	3085
6	,, ,, ...	3260	3067
4	,, ,, ...	3265	3062

0·216 gram in 1000 c.c.

Thickness of layer of liquid n millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
20	Spectrum transmitted to	3290	3039
10	,, ,, ...	3340	2993
8	,, ,, ...	3355	2980
	Absorption band..................	**3355—3980**	**2980—2512**
	Spectrum transmitted	3980—4160	2512—2403
6	,, ,, to	3365	2971
	Absorption band..................	**3365—3910**	**2971—2557**
	Spectrum transmitted	3910—4235	2557—2361
4	,, ,, to	3390	2947
	Absorption band..................	**3390—3900**	**2947—2563**
	Spectrum transmitted	3900—4300	2563—2324
2	,, ,, to	3420	2923
	Absorption band..................	**3420—3800**	**2923—2631**
	Spectrum transmitted	3800—4470	2631—2236
1·5	,, ,, to	3470	2881
	Absorption band..................	**3470—3750**	**2881—2666**
	Spectrum transmitted	3750—4500	2666—2221
1	Spectrum weak	3500—3700	2856—2702
	Spectrum transmitted to	4530	2207

Ethyl Diacetylsuccinate, $CO_2Et{\cdot}CHAc{\cdot}CHAc{\cdot}CO_2Et$.

This substance was obtained from Kahlbaum in the form of quite white and well-formed crystals melting at 87°.

Free Ester.

0·27 gram (1 milligram-molecule) in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3370	2966
20	,, ,, ...	3405	2935
10	,, ,, ...	3470	2881
8	,, ,, ...	3500	2856
6	,, ,, ...	3533	2829
4	,, ,, ...	3560	2808

0·27 gram in 1000 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3570	2801
20	,, ,, ...	3590	2786
10	,, ,, ...	3680	2717
8	,, ,, ...	3720	2687
6	,, ,, ...	3770	2652
4	,, ,, ...	3840	2603

0·27 gram in 10,000 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3870	2583
20	,, ,, ...	4030	2480
10	,, ,, ...	4295	2328
8	,, ,, ...	4375	2285
6	,, ,, ...	4490	2227

Ester in presence of Alkali Hydroxide.

0·27 gram in 10,000 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3193	3131
20	,, ,, ...	3270	3057
	Absorption band	**3270—4000**	**3057—2499**
	Spectrum transmitted	4000—4240	2499—2358
15	,, ,, to	3340	2993
	Absorption band	**3340—3840**	**2993—2603**
	Spectrum transmitted	3840—4400	2603—2272
10	,, ,, to	3400	2940
	Absorption band	**3400—3800**	**2940—2631**
	Spectrum transmitted	3800—4400	2631—2272
8	,, ,, to	3455	2893
	Absorption band	**3455—3740**	**2893—2673**
	Spectrum transmitted	3740—4490	2673—2227
6	Spectrum weak	3500—3700	2856—2702
	Spectrum transmitted to	4520	2212

Ethyl Benzoylsuccinate, $CO_2Et{\cdot}CH(COPh){\cdot}CH_2{\cdot}CO_2Et$.

This substance was obtained from Kahlbaum, and was perfectly colourless. The absorption curves of the ester in the free state and in the presence of 1, 10, 20, and 100 equivalents are shown in Fig. 2, curves 1, 2, 3, 4, 5 respectively.

Acetonylacetone.

0·114 gram (1 milligram-molecule) in 100 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3960	2525
20	,, ,, ...	4030	2480
10	,, ,, ...	4110	2432
8	,, ,, ...	4150	2409
6	,, ,, ...	4205	2377
4	,, ,, ...	4280	2335
3	,, ,, ...	4360	2293

Hydroxymethylenecamphor.

This substance was kindly supplied to us by Dr. M. O. Forster.

0·180 gram (1 milligram-molecule) in 100 c.c. of alcohol.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3060	3267
20	,, ,, ...	3128	3196
10	,, ,, ...	3335	2997
8	,, ,, ...	3355	2979
6	,, ,, ...	3370	2966
4	,, ,, ...	3391	2948

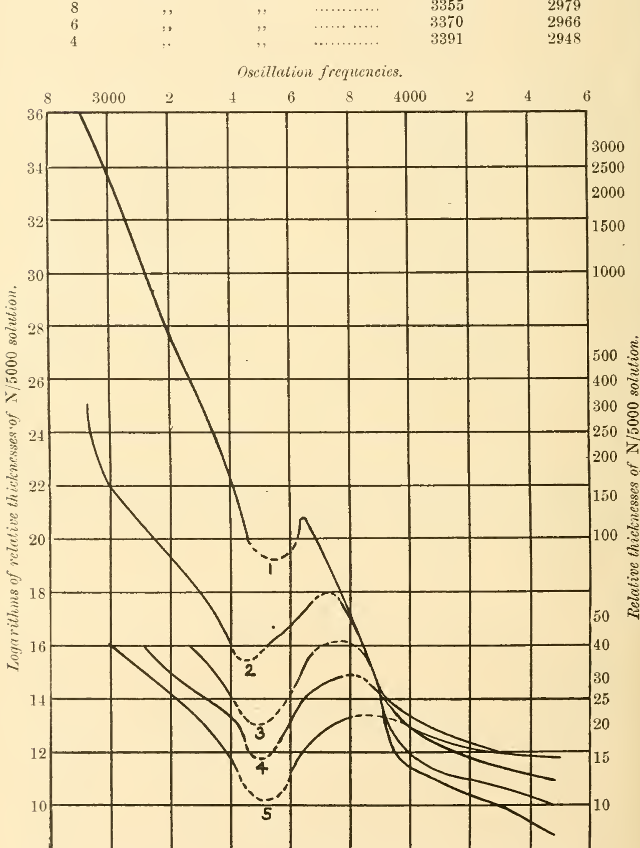


Fig. 2.

0·180 gram in 1000 c.c.

Thickness of layer of liquid in millimetres.	Description of spectrum.	$^1/\lambda$.	λ.
30	Spectrum transmitted to	3400	2941
20	,, ,, ...	3430	2914
10	,, ,, ...	3470	2881
8	,, ,, ...	3490	2864
6	,, ,, ...	3518	2841
4	,, ,, ...	3553	2814
3	,, ,, ...	3650	2739
2·5	,, ,, ...	3810	2624
2·2	,, ,, ...	4140	2415
2	,, ,, ...	4295	2327
1·5	,, ,, ...	4400	2272

Conclusions.

In discussing the conclusions which may be drawn from these results it must at once be mentioned that they only refer to the conditions under which the substances exist in solutions of concentrations varying from $N/100$ to $N/10,000$; whether the same conditions exist with the pure substances cannot, of course, be definitely concluded from our experiments. There is, however, no reason why the constitution of the pure substance should be expected to differ materially from that in solution.

The following conclusions may be drawn:

1. In the case of the aliphatic tautomeric substances, neither the pure ketonic nor the pure enolic form gives an absorption band.

2. In solutions of the strengths dealt with by us the pure ketonic form is almost diactinic, whilst the pure enolic form exerts a small general absorption.

3. When an absorption band is given, it means that the ketonic and enolic forms are coexistent and in dynamic equilibrium with one another—that is to say, a number of the molecules are oscillating between the two conditions.

4. The persistence of the absorption band, that is to say, the relative change of dilution or of thickness of the solution during which the absorption band can be observed, is a measure of the number of molecules in the changing state.

4a. In order that the absorption band may be developed it is probably necessary that a considerable number of the molecules must be in the changing state.

5. The addition of alkali tends to increase the persistence of the band, whilst the addition of acid tends to decrease it.

6. The successive increase of alkali increases the persistence of the band until a maximum is reached, beyond which the further addition of alkali does not increase it.

7. The absorption bands are given by the aluminium derivatives of the tautomeric substances as well as by their sodium derivatives; the former compounds are soluble in alcohol, and are neither hydrolysed nor ionised.

8. The oscillation-frequency of the absorption band bears no relation to the mass of the atom in the labile state.

9. The absorption band is due to the change of linking accompanying the change from the one form to the other, and its formation may be explained by the modern physical conception of the atom as a system of electrons.

10. The labile atom may be regarded as a potential ion, inasmuch as the bond of attraction or Faraday tube of force must be considered to be lengthened sufficiently to allow of the interchange of the atom from the one position to the other within the molecule; the action of alkali and acid may thus be considered to have the effect of lengthening or shortening these tubes of force, thereby increasing or decreasing the number of interchanges taking place in unit time.

11. This view may be taken of salts in solution, that the bonds of attraction connecting the "ions" together are lengthened by the solvent. When the length of the Faraday tubes is below a certain critical length, the salt is "non-ionised." When the average length of the tubes of force is equal to or a little less than the critical length, a few interchanges of ions between adjacent molecules take place, and the salt is partially ionised. When the length of the Faraday tubes is greater than the critical value, then perfectly free interchange takes place between the ions of different molecules, and the salt is completely "ionised."

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LXXIX.—*The Basic Properties of Oxygen at Low Temperatures. Additive Compounds of the Halogens with Organic Substances containing Oxygen.*

By DOUGLAS McINTOSH.

THE formation and decomposition of chemical compounds are greatly influenced by temperature. Many compounds formed at low temperatures are decomposed at higher, and decomposition is usually asso-

ciated with a change of valency in one or more of the elements forming the compound. In the case of the chlorides of phosphorus, the pentachloride at a high temperature is broken up, yielding the trichloride, and the valency of the phosphorus is said to change from five to three. It is, however, not necessary that a compound should be decomposed to bring about a change in valency. Liquids, such as acetic acid and water, polymerise, and this polymerisation is lessened by a rise in temperature. Here, doubtless, the valency of some element is lowered and smaller molecules result.

An interesting case of change in valency is exhibited by iodine; as the temperature is raised, the molecular weight of the vapour becomes less, until at 1400° it equals 127. At this temperature, iodine does not combine with the elements with which it unites at lower temperatures; it is inert and similar to the elements of the helium group. As the temperature is lowered, the iodine molecule changes from I to I–I, from the valency of 0 to 1. It is possible that a similar change may take place in the elements of the helium group if sufficiently low temperatures are employed, but the experiments of Baly and Donnan (Trans., 1902, **81**, 907) show no polymerisation in the case of liquid argon.

It has been pointed out (Walker, McIntosh, and Archibald, Trans., 1904, **85**, 1098) that some organic substances containing oxygen unite with the halogen hydrides and that definite compounds are formed. Archibald and McIntosh have shown (Trans., 1904, **85**, 919) that the amount of acid uniting with one molecule increases as the temperature decreases until substances such as $(CH_3)_2O,5HCl$ are produced, and from the great amount of heat given out during combination have inferred that the whole of the hydrogen chloride existed in the compound as an integral part of the molecule and not as "acid of crystallisation." If the hydrogen chloride attaches itself to the oxygen, and if the chlorine is regarded as a monad, the valency of the oxygen must be twelve. But since liquefied hydrogen chloride, unlike the corresponding bromide and iodide, polymerises, the chlorine may with equal justice be viewed as a tervalent, and the oxygen as a quadrivalent element.

To test this point, the compounds of methyl ether and alcohol with hydrogen bromide and iodide have been investigated (*J. Amer. Chem. Soc.*, 1905, **27**, 26) in the hope of obtaining substances melting at a low temperature, in which the oxygen has a valency greater than six. The compounds, however, melted at a comparatively high temperature and showed the oxygen to be a tetrad, and as these substances were the most likely for the purpose mentioned above, it seemed impossible that any organic substance with the hydride of bromine or iodine would give compounds of the type desired.

The ready solubility of chlorine and bromine in the alcohols and ethers of the fatty series leads to the conclusion that if compounds are formed they will crystallise out at a low temperature. These products might be analogous to the hydrates of chlorine and bromine, or might be compounds in which the halogen was attached to the oxygen atom, and so a test of the limiting valency of oxygen might be made.

Experiments have now been made with typical substances of the six classes of the fatty series containing carbon, hydrogen, and oxygen, and the compounds obtained are, I believe, new. Other additive compounds of the same series have been prepared at higher temperatures, and will be referred to in the final table.

Materials.

The alcohols were dehydrated by quicklime and copper sulphate; the ethers by sodium or by distillation over phosphoric oxide. The acetone was redistilled, the acetaldehyde prepared from para-acetaldehyde, and the acetic acid recrystallised several times. The ethyl acetate was cooled to -80°, and filtered from the acetic acid and water which solidified; it contained alcohol, but in too small a proportion to affect the analyses of the compounds obtained. The chlorine, made from hydrochloric acid by means of chromic acid, was passed through water and a tube containing crystallised copper sulphate to remove the hydrogen chloride, dried by phosphoric oxide, and condensed by the aid of solid carbon dioxide and ether.

Preparation and Analysis of Compounds.

The organic liquid was cooled to -80° and chlorine added at the same temperature. The solution was accompanied by the evolution of a small amount of heat, due probably to the formation of the compound. In the case of bromine, the solid was used at -80°, or the liquid halogen was added slowly from a dropping funnel. The bromine dissolved with a slight development of heat, and after some few minutes a solid began to crystallise out.

The compounds exhibit properties which differ greatly from the analogous substances formed from the halogen hydrides. Their formation takes place with only a slight evolution of heat; they do not readily form supersaturated solutions, and their separation is apparently not influenced by the presence of the solid phase. They can be obtained in long needles or prisms, are but sparingly soluble in the organic substance from which they are prepared, and have definite melting points above which temperature substitution often

begins, accompanied by much development of heat, and as the temperature rises this action goes on with increasing acceleration.

A number of experiments were made to determine the extent of the substitution in a liquid treated with chlorine or bromine in the manner described above, by destroying the halogen and titrating the acid with alkali, using phenolphthalein as indicator. The acid never amounted to more than 0·3 per cent. If substitution is allowed to occur to an appreciable extent, it seems impossible to isolate the compound in the crystalline state. This peculiarity in an ether-bromine compound has been noticed by Schützenberger.

Unless otherwise indicated, each compound was washed with its organic constituent and dried by suction in a jacketed filter tube at a temperature of about $-80°$ or, if necessary, $-95°$. In general, the amount of halogen found will be low on account of the absorption of the other constituent, which has generally a low vapour pressure. With the alcohol-bromine compound, we shall have the alcohol and bromine in equilibrium with the additive substance:

$$C_2H_5HO + Br \rightleftarrows C_2H_5HOBr.$$

As the alcohol and the bromine are removed, more of the compounds will be decomposed to maintain the equilibrium. The amount of alcohol occluded can be brought down to a certain point depending on the relative vapour pressures of the bromine, the alcohol, and the compound, but cannot be completely removed. In this case, the vapour pressure of the bromine is higher than the alcohol, and so the latter will be in excess.

The samples for analysis were removed from the filter at intervals of about ten minutes, and when brought into contact with a potassium iodide solution were instantly decomposed, the liberated iodine being determined with decinormal sodium thiosulphate. All analyses made are recorded.

Alcohol Compounds.

A crystalline compound of methyl alcohol and chlorine was obtained, melting at $-96°$ (chlorine melts at $-102°$ and methyl alcohol at $-95°$). On account of its low melting point, the product was not analysed, but its composition is probably CH_4OCl.

Ethyl alcohol gave a similar compound melting at $-88°$. One preparation only was analysed, giving 43·7 and 44·9 per cent. of chlorine. C_2H_6OCl requires 43·6 per cent. chlorine.

Methyl alcohol and bromine gave a light red crystalline compound, melting at $-53°$. Three preparations were analysed.

No. of preparation analysed.	Bromine found.	No. of preparation analysed.	Bromine found.
I	67·4 per cent.	III...........	69·7 per cent.
	67·5 ,,		69·3 ,,
II	68·7 ,,		69·4 ,,
	69·1 ,,		69·7 ,,
	71·5 ,,		
	72·3 ,,		

CH_4OBr_2 and CH_4OBr require Br = 83·3 and Br = 71·4 per cent. respectively. The compound, consequently, is CH_4OBr.

Ethyl alcohol and bromine gave a compound melting at − 45°. The analyses gave 76·5, 78·0, 77·4, 77·3; mean Br = 77·3 per cent.; $C_2H_6OBr_2$ requires Br = 77·7 per cent.

An attempt to reproduce this compound was made with the following results. The compound melted at − 61°.

No. of preparation analysed.	Bromine found.	No. of preparation analysed.	Bromine found.
I	57·3 per cent.	III	58·4 per cent.
	57·5 ,,		56·8 ,,
	57·9 ,,		57·2 ,,
	58·2 ,,		54·6 ,,
Mean......	57·7 ,,	Mean......	57·3 ,,
II	56·9 ,,		
	56·7 ,,		
	59·0 ,,		
	57·5 ,,		
Mean......	57·5 ,,		

or for the three preparations, Br = 57·5 per cent., which corresponds roughly with C_2H_6OBr.

It might be thought that bromine was precipitated with the first compound, and that chance was responsible for the close approximation to the formula $C_2H_6OBr_2$, but this could not have been the case, since the product was washed several times with alcohol. Perhaps C_2H_6OBr and $C_2H_6OBr_2$ may both exist, and the temperature at which the phases are in equilibrium may be near − 80°. The proper temperature might have been maintained during one experiment and the $C_2H_6OBr_2$ precipitated.

Ether Compounds.

No solid product could be obtained from methyl ether and chlorine even at a temperature of − 95°. Since heat is developed it seems probable that a compound would be obtained if the temperature were lowered sufficiently

With bromine, beautiful red needles, which melted at − 68°, were precipitated. The analysis of one preparation gave 78·4, 79·0,

79·1, 79·3; mean Br = 78·9 per cent., whilst the compound $(CH_3)_2OBr_2$ requires Br = 77·7 per cent.

In these analyses, the amount of the halogen was greater than the theoretical, although the substance was washed with methyl ether. The explanation is simple. At −80°, the methyl ether has probably a higher vapour pressure than the bromine. Methyl ether was removed by the air until the equilibrium point was reached, and so an excess of bromine was present.

Ethyl ether and chlorine yielded a white, crystalline product melting at −51°.

No. of preparation analysed.	Chlorine found.	No. of preparation analysed.	Chlorine found.
I	42·1 per cent.	III	43·6 per cent.
	40·5 ,,		45·7 ,,
	43·7 ,,		
	42·1 ,,	IV	45·1 ,,
Mean......	42·1 ,,		45·5 ,,
II	44·4 ,,		
	45·4 ,,		
	43·2 ,,		
	42·7 ,,		
Mean......	43·9 ,,		

(Preparations I and II were washed with ether; III and IV with liquefied chlorine).

$C_4H_{10}OCl$ and $C_4H_{10}OCl_2$ require 32·4 and 48·9 per cent. of chlorine respectively; hence the product has the latter formula.

Bromine and ether gave long, reddish-yellow needles, melting at −40°.

No. of preparation analysed.	Bromine found.	No. of preparation analysed.	Bromine found.
I	66·3 per cent.	II	65·8 per cent.
	64·8 ,,		67·0 ,,
	65·9 ,,		64·1 ,,
	67·5 ,,		66·7 ,,
Mean......	66·1 ,,	Mean......	65·9 ,,

$C_4H_{10}OBr_2$ contains 68·4 per cent. of bromine and the compound, therefore, consists of one molecule of ether and two atoms of bromine.

Schützenberger (*Annalen*, 1873, **167**, 86) described a compound of bromine and ether, $C_4H_{10}OBr_3$, melting at 22°; this substance was easily prepared by following Schützenberger's directions, but it was not analysed.

Acetone Compound.

A white, crystalline compound, melting at $-53°$, appears immediately on mixing acetone and chlorine. The analytical results were:

No. of preparation analysed.	Chlorine found.	No. of preparation analysed.	Chlorine found.
I	49·4 per cent.	II	55·5 per cent.
(washed with	51·4 ,,	(washed with	55·8 ,,
acetone)	52·0 ,,	chlorine)	54·2 ,,
	51·1 ,,		54·5 ,,
Mean......	51·0 ,,	Mean......	55·0 ,,

C_3H_6OCl and $C_3H_6OCl_2$ require 37·9 and 55·0 per cent. of chlorine respectively; the substance has therefore the latter formula.

Bromine gave a light yellow compound, which, on account of its high melting point ($-12°$), could be easily dried.

No. of preparation analysed.	Bromine found.	No. of preparation analysed.	Bromine found.
I	67·4 per cent.	II	68·5 per cent.
	66·2 ,,		67·2 ,,
	70·5 ,,		64·7 ,,
	71·1 ,,		68·9 ,,
Mean......	68·8 ,,	Mean......	67·3 ,,

A compound consisting of one molecule of acetone and two atoms of bromine would contain 73·4 per cent. of bromine, whilst one composed of two molecules of acetone and three atoms of bromine require $Br = 67·4$ per cent. It was inferred, from the above analyses, that the product was $(C_3H_6O)_2Br_3$. But this compound, although apparently perfectly dry, occluded a large amount of acetone. Taking advantage of some very cold weather, the product was dried and weighed out of doors.

Analysis of two specimens gave the following results:

No. of preparation analysed.	Bromine found.
III..................	68·6, 69·7 per cent.
IV..................	71·5, 72·5 ,,

(Preparation III was dried by suction; preparation IV by pressing between layers of filter paper).

The formula is, therefore, $C_3H_6OBr_2$.

Ethyl Acetate Compounds.

With ethyl acetate and chlorine, a compound melting at $-64°$ was obtained.

No. of preparation analysed.	Chlorine found.	No. of preparation analysed.	Chlorine found.
I	51·4 per cent.	II	55·7 per cent.
(washed with	50·9 ,,	(washed with	55·3 ,,
ethyl acetate)	51·8 ,,	chlorine)	54·8 ,,
	52·7 ,,		54·4 ,,
Mean......	51·7 ,,	Mean......	55·0 ,,

This compound is therefore $CH_3{\cdot}CO_2{\cdot}C_2H_5Cl_3$, which contains 54·7 per cent. of chlorine.

With bromine, a red compound, melting at $-39°$, is easily prepared. The analytical results for one preparation were 70·5, 71·6, 69·5, 70·2 ; mean Br = 70·5 per cent., whilst compounds consisting of one molecule of ethyl acetate to two atoms of bromine and one of ethyl acetate to three atoms of bromine require 64·5 and 73·2 per cent. respectively. The formula is, therefore, $CH_3{\cdot}CO_2{\cdot}C_2H_5Br_3$.

Compounds with Aldehydes.

Acetaldehyde shows evidence of forming compounds with the halogens, a small amount of heat being evolved in the addition, which is similar, apparently, to those reactions previously mentioned. But these compounds are soon broken up, and para- and meta-acetaldehydes are produced with a very great heat evolution. This "catalytic" change is brought about with very great rapidity by means of the smallest quantity of iodine ; the reaction is slower with bromine, and very much slower with chlorine. The chlorine compound, which was probably very impure, melted at $-11°$. It was washed with liquid chlorine and seemed dry when taken for analysis. The results were 31·1 and 30·4 per cent. chlorine. $(CH_3{\cdot}CHO)_2,Cl$ and $(CH_3{\cdot}CHO)_3Cl_2$ require 28·7 and 35·0 per cent. of chlorine respectively.

When left in the filter tube for twenty minutes, the percentage of chlorine fell to 27, and after an hour to 3. The dry cold air had removed nearly all the chlorine, and impure para-acetaldehyde, melting at 6°, remained.

With a second preparation, three analyses gave 32·1, 30·2, and 32·4 per cent. of chlorine. The halogen was completely removed after passing dry air over the substance for an hour.

Compounds with Acetic Acid.

This acid, melting at 16°, is only slightly soluble in bromine or chlorine. Solutions were made in various solvents, such as alcohol, and the halogen was added to these mixtures. A compound was undoubtedly formed in both cases, but was contaminated with acetic acid. The analyses indicated, in general, ratios varying between two and three molecules of the acid to one atom of the halogen—results which may be far from the truth.

In the following table are placed the results of the experiments described above, together with the formulæ of the additive halogen compounds described by others, and the approximate temperatures at which these substances melt. No general rule can be given for the influence of temperature on the amount of the halogen added. Chlorine and bromine unite in the same proportion with the organic compounds, and the oxygen atoms retain the power of taking up the same number of halogen atoms over a wide range of temperature. Hydroxylic oxygen unites with one atom of a halogen; ketonic and ethereal oxygen with two. No doubt a large number of compounds belonging to these series could be produced at other temperatures.

Collected Results.

Compound.	M. p.	Compound.	M. p.
* $(H_2O)_8Cl_2$	8°	$C_3H_6OCl_2$	−53°
† $(H_2O)_{10}Br_2$	6	$C_3H_6OBr_2$	−12
CH_4OCl (?)	−96	$CH_3{\cdot}CO_2{\cdot}C_2H_5,Cl_3$	−64
C_2H_6OCl	−88	$CH_3{\cdot}CO_2{\cdot}C_2H_5,Br_3$	−39
CH_4OBr	−55	¶ $(CH_3{\cdot}CO_2{\cdot}C_2H_5)_2,Br_3$	—
C_2H_6OBr	−61	‖ $CH_3{\cdot}CO_2{\cdot}C_2H_5,Br_2$	—
$(CH_3)_2OBr_2$	−68	$(CH_3{\cdot}CHO)_3,Cl_2$ (?)	−11
$C_4H_{10}OCl_2$	−51	§ $(C_2H_4O_2Br)_2,HBr$	8
$C_4H_{10}OBr_2$	−40	§ $(C_2H_4OBr)_2,HCl$	8
‡ $C_4H_{10}OBr_3$	+22		

* Roozeboom, *Rec. Trav. chim.*, 1884, **3**, 59; 1885, **4**, 69.

† *Ibid.*, 1884, **3**, 73; 1885, **4**, 71.

‡ Schützenberger, *Annalen*, 1873, **167**, 86.

¶ and ‖ Distillates of constant compositions. Schützenberger, *Ber.*, 1873, **6**, 71; Kraft, *Annalen*, 1864, **129**, 50.

§ Hell and Mühlhäusen, *Ber.*, 1878, **11**, 244; Steiner, *ibid.*, 1874, **7**, 184.

Although the constitutions of compounds are, in general, only of value in so far as they are determined through chemical reactions, it seems worth while to endeavour to fix the probable constitutions of some of the typical compounds described above, and whilst it may be argued that these substances are "molecular compounds" and do not differ from salts with water or alcohol of crystallisation, they are, at

least, less complex. Some of the liquids used in forming the compounds are highly associated, as, for example, the alcohols, whilst others, such as the ethers, consist of simple molecules. The additive compounds are formed from members of these two classes with equal readiness and the association of the constituents does not affect the constitutions.

In the classes of substances studied, oxygen is, under certain conditions, quadrivalent at low temperatures, and the halogens are probably tervalent elements. From the foregoing formulæ, it seems impossible to give to oxygen a higher valency than four, and in the constitutions of the compounds described above one may regard oxygen and bromine * as having valencies of four and three respectively.

The dibromine-ether compound may have the graphical formula $C_4H_{10}O{<}^{Br}_{Br}$, but with the tribromine compound, in order that all the linkings may be satisfied, it is necessary to double the formula. If this is done in both cases, the constitution for the dibromine-ether will be $C_4H_{10}O{:}Br{\cdot}Br{:}Br{\cdot}Br{:}OC_4H_{10}$, and similarly with the tribromine compound.

If the second constitution is correct, it is probable that the substance will not be ionised, for there is no place where the molecule can dissociate and yield ions. The molecular conductivity in a $3/N$-solution was only 0·002, but perhaps better conduction could not be expected in a non-ionising medium such as ether.

The alcohol-bromine compound probably has the constitution $CH_4O{:}Br{\cdot}Br{:}Br{\cdot}Br{:}OCH_4$, and here, too, we could not expect ionisation. Its solution gave a molecular conductivity of 0·006, which might easily be accounted for by the formation of small amounts of hydrogen bromide.

The formula of the ketone compound must be doubled and we shall have for the bromine-ketone derivative, $C_3H_6O{:}Br{\cdot}Br{:}Br{\cdot}Br{:}OC_3H_6$.

Liquid ethyl acetate is, according to Ramsay and Shields, an unassociated substance, and we may regard it as containing a hydroxyl and a ketonic oxygen atom. If these atoms are, as regards their powers of forming additive compounds, independent, we shall expect ethyl acetate to take up three atoms of bromine or chlorine, since the hydroxylic oxygen atom takes up one halogen atom, and the ketonic oxygen two. This we find to be the case.

The constitution might then be expressed by doubling the formula, and having a single linking between the two bromine atoms attached to the hydroxylic oxygen atoms.

Organic chemistry has for many years been mainly the chemistry

* Aston and Ramsay (Trans., 1904, 65, 167) show that liquid bromine is Br_2, but it is impossible to say whether the linking in the molecule is single or triple.

of substitution brought about generally by high temperatures. Another side of organic chemistry—not without interest—is the study of additive products which are formed at low temperatures. A few of these compounds have been described, but many more may exist, the study of which might help to solve some of the problems of organic * and inorganic chemistry.

In conclusion, I wish to express my thanks to Dr. B. J. Harrington and to Dr. J. W. Walker for advice and interest shown during the progress of this research.

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LXXX.—*The Constitution of Pilocarpine. Part V. Conversion of* iso*Pilocarpine into Pilocarpine.*

By HOOPER ALBERT DICKINSON JOWETT.

ALTHOUGH the constitutional formula of *iso*pilocarpine,

$$\begin{array}{l} C_2H_5\cdot CH\cdot CH\cdot CH_2\cdot C\cdot N(CH_3) \\ \qquad\;\; | \qquad | \qquad\qquad\;\; \| \qquad\qquad\quad > CH, \\ \qquad CO \;\; CH_2 \quad\;\; HC\text{———}N \\ \qquad\;\; \diagdown\;\diagup \\ \qquad\quad\; O \end{array}$$

may be considered to be established, the relation between the two isomeric alkaloids, pilocarpine and *iso*pilocarpine, cannot be regarded as settled. In a previous communication (Trans., 1903, **83**, 438), this question was discussed, and it was shown that the evidence on the whole favoured the view that the alkaloids were stereoisomerides. The chief arguments in favour of this view are (1) the great similarity both in chemical properties and physiological action existing between the alkaloids; (2) the ease of conversion of pilocarpine into *iso*pilocarpine; (3) the fact that the absorption spectra of the nitrates of the two alkaloids are absolutely identical; and (4) that it is difficult to account for the isomerism on structural grounds. On the other hand, the arguments against stereoisomerism and in favour of structural isomerism were (1) the difference in behaviour of the alkaloids towards bromine and water at 100° under pressure, when, in the case of pilocarpine, bromocarpinic acid, $C_{10}H_{15}O_4N_2Br$, was produced, whilst with *iso*pilocarpine dibromo*iso*pilocarpinic acid, $C_{11}H_{14}O_4N_2Br_2$, was formed;

* See Nef, *J. Amer. Chem. Soc.*, 1904, **26**, 1549

and (2) the difference in their behaviour towards chromic acid, pilocarpine yielding pilocarpoic acid, $C_{11}H_{16}O_5N_2$, whilst in the case of *iso*pilocarpine no definite product could be isolated.

With regard to the first argument, it was pointed out that the apparent difference in the action of bromine might be accounted for by assuming that a similar reaction occurred in each case, but that the isomeric products differed in their facility of crystallising ; in each case the yield of crystalline acid is small, thus proving that the substance isolated does not represent the whole product of the reaction, and furthermore the alkaloids are known to yield isomeric substances differing in their ability to crystallise, for example, pilocarpine methiodide is amorphous, whilst *iso*pilocarpine methiodide is crystalline. Thus it is possible that bromocarpinic acid is crystalline, whilst bromo*iso*carpinic acid is amorphous, and dibromopilocarpinic acid amorphous, whilst the corresponding isomeride is crystalline.

With respect to the second argument, it was shown (*loc. cit.*) that the reaction of pilocarpine with chromic acid had not been sufficiently studied to admit of any deduction being made in favour of either theory. In the meantime, the action of chromic acid on pilocarpine and the properties of the two bromo-acids above mentioned have been further studied by Pinner (*Ber.*, 1905, 38, 1510). He, however, is of opinion that the isomerism is not due solely to stereochemical causes, but that the alkaloids are structural isomerides, and that this isomerism depends on the point of attachment of the pilopic complex, $C_7H_{11}O_2$, to the glyoxaline ring. But as I have previously pointed out, there are several objections to this explanation.

The three possible formulæ are :

$$\begin{array}{l} C_7H_{11}O_2\cdot C\cdot N(CH_3) \\ \quad\;\; HC \text{------} N \end{array} \!\!>\! CH \; : \qquad \begin{array}{l} \qquad\quad\;\; HC\cdot N(CH_3) \\ C_7H_{11}O_2\cdot C \text{------} N \end{array} \!\!>\! CH \; :$$
$$\qquad\text{I.} \qquad\qquad\qquad\qquad\qquad \text{II.}$$

$$\begin{array}{l} HC\cdot N(CH_3) \\ HC \text{------} N \end{array} \!\!>\! C\cdot C_7H_{11}O_2 \; .$$
$$\text{III.}$$

If I be accepted as the constitutional formula for *iso*pilocarpine, then pilocarpine must be represented by formula II or III. But II is so similar to I that it would not explain the apparent difference in the behaviour of the alkaloids towards bromine or chromic acid, whilst III is, as Pinner admits, improbable, for it is difficult to conceive how the group $C_7H_{11}O_2$ could pass from the carbon atom to the other as required in formula I.

Furthermore, if such a change took place in the case of the grouping such as $C_7H_{11}O_2$, one would expect it to occur with greater facility

when this complex is replaced by a simpler group such as CH_3. But the three glyoxalines of the following formulæ are known:

$$\begin{matrix} CH_3{\cdot}C{\cdot}N(CH_3) \\ \| \\ HC\text{———}N \end{matrix}\!\!>\!CH \; : \; \begin{matrix} HC{\cdot}N(CH_3) \\ \| \\ CH_3{\cdot}C\text{———}N \end{matrix}\!\!>\!CH \; : \; \begin{matrix} HC{\cdot}N(CH_3) \\ \| \\ HC\text{———}N \end{matrix}\!\!>\!C{\cdot}CH_3,$$

and in the course of their preparation have been distilled at a somewhat high temperature (above 200°). Therefore no such change occurs with these simple glyoxalines, and it is unlikely that a group such as $C_7H_{11}O_2$ would migrate when the simple CH_3 group shows no such tendency.

Pinner's recent work also affords an explanation of the apparent difference in the reaction of the alkaloids with chromic acid. He has shown that pilocarpoic acid can be converted into the isomeric *iso*-pilocarpoic acid by means exactly analogous to those employed for converting pilocarpine into *iso*pilocarpine, and there is little doubt that the same relation exists between the isomeric acids as between the alkaloids. The failure to isolate the *iso*pilocarpoic acid from the reaction of *iso*pilocarpine with chromic acid would therefore appear to be due solely to experimental difficulties.

Pinner's chief argument against stereoisomerism is open to serious objection. He states, "The conversion of pilocarpine and its derivatives into the *iso*-form cannot be simply a stereochemical rearrangement, but must consist in a change in the arrangement of the atoms to each other. For stereochemical isomerism is only possible in the complex

$$\begin{matrix} C_2H_5{\cdot}CH{\cdot}CH{\cdot}CH_2{\cdot} \\ \quad | \qquad | \\ \quad CO \;\; CH_2 \\ \quad \diagdown \diagup \\ \quad O \end{matrix}$$

As a matter of fact, one always obtains isomeric compounds from pilocarpine and *iso*pilocarpine so long as the glyoxaline ring remains intact. As soon as compounds are formed in which this group no longer exists, it is immaterial whether pilocarpine or *iso*pilocarpine is selected as the initial material. Consequently the isomerism cannot exist in the complex

$$\begin{matrix} C_2H_5{\cdot}CH{\cdot}CH{\cdot}CH_2{\cdot} \\ \quad | \qquad | \\ \quad CO \;\; CH_2 \\ \quad \diagdown \diagup \\ \quad O \end{matrix}$$

, but must be in the glyoxaline ring,

$$\begin{matrix} {\cdot}C{:}N(CH_3) \\ \| \\ HC\text{———}N \end{matrix}\!\!>\!CH."$$

Pinner's argument, therefore, is that if the isomerism is in the $C_7H_{11}O_2$ complex one ought to obtain isomeric homopilopic and pilopic acids corresponding to pilocarpine and *iso*pilocarpine. Whereas both alkaloids yield on oxidation the same homopilopic acid. But this fact is readily explained when it is considered that the homopilopic or pilopic acid is formed in the presence of alkali, and is purified by the

distillation of its ester, both of which conditions would ensure conversion into the *iso*-form.

The only valid argument against stereoisomerism and in favour of structural isomerism seems to be the apparent difference in the behaviour of the alkaloids towards bromine at 100°, but the explanation offered for this appears to be satisfactory. However, more experimental evidence on this point is desirable, and the investigation of the action of bromine under similar conditions on the different dimethylglyoxalines should throw some light on the subject, and this inquiry is already in hand.

There seemed to be one experiment which would almost settle the question of the nature of the isomerism. If the alkaloids are stereoisomerides, then the conversion of pilocarpine into *iso*pilocarpine should not be complete, but a state of equilibrium should result. By acting on *iso*pilocarpine under the conditions which convert pilocarpine into *iso*pilocarpine, for example, heating with alkali, the same state of equilibrium should be formed, and it should then be possible to isolate some pilocarpine from this mixture.

If, on the other hand, the alkaloids are structural isomerides, this reverse change should not be possible. For it must be assumed that one isomeride, namely, *iso*pilocarpine, is the more stable under the conditions of experiment, and, as no possibility seems to exist for tautomerism, then this more stable isomeride could not pass into a less stable one by the reagent which has already produced the more stable isomeride.

This experiment would therefore appear to definitely settle the question, for if *iso*pilocarpine could not be converted by alkali into pilocarpine then the isomerism cannot be solely stereochemical, but if this conversion does take place, then structural isomerism is extremely improbable, and the isomerism must be due to the racemisation of the asymmetric carbon atom adjacent to the carboxyl group. The relation between the alkaloids might thus be represented as follows :

$$\begin{array}{l} C_2H_5\cdot\overset{+}{C}H\cdot\overset{+}{C}H\cdot CH_2\cdot C\cdot N(CH_3) \\ \quad\quad\;\; | \quad\;\; | \quad\quad\quad\;\; \| \\ \quad\quad CO \;\; CH_2 \quad HC \text{———} N \\ \quad\quad\;\; \diagdown \;\; \diagup \\ \quad\quad\quad\;\; O \end{array} \!\!>\! CH \;:$$

Pilocarpine.

$$\begin{array}{l} C_2H_5\cdot\overset{-}{C}H\cdot\overset{+}{C}H\cdot CH_2\cdot C\cdot N(CH_3) \\ \quad\quad\;\; | \quad\;\; | \quad\quad\quad\;\; \| \\ \quad\quad CO \;\; CH_2 \quad HC \text{———} N \\ \quad\quad\;\; \diagdown \;\; \diagup \\ \quad\quad\quad\;\; O \end{array} \!\!>\! CH.$$

*iso*Pilocarpine.

A quantity of pure *iso*pilocarpine nitrate (m. p. 159°; $[\alpha]_D + 35.7°$) was recrystallised from alcohol, and the mother liquors evaporated to a small bulk. The crystals which separated from the mother liquor melted at 159°, thus proving the homogeneity of the salt.

Fifty grams of the nitrate first mentioned were converted into the base, dissolved in alcohol, 30 grams of potassium hydroxide in alcoholic solution added, and the whole heated on a water-bath in a reflux apparatus for 3 hours. The base was regenerated and converted into the nitrate, which was then fractionally crystallised. The first fraction (40 grams) melted at 159°, and had $[\alpha]_D + 36.2°$. It was therefore pure *iso*pilocarpine nitrate.

From the mother liquors, two crops of crystals were obtained, both of which melted at 144° and had $[\alpha]_D + 58.7°$. As the melting point of these two crops of crystals was not altered by recrystallisation, they were converted into the hydrochloride and then crystallised from absolute alcohol. After three recrystallisations, a product was obtained melting at 201°, and a determination of its specific rotation in water gave $\alpha_D + 1°44'$; $l = 2$ dcm.; $c = 0.9336$; $[\alpha]_D + 92.8°$.

Pilocarpine hydrochloride melts at 204° and has $[\alpha]_D + 91.7°$.

In order to finally prove the identity of this substance with pilocarpine, the hydrochloride was converted into the nitrate. The nitrate melted at 177—178°, and the melting point was unchanged when mixed with an equal quantity of pilocarpine nitrate.

The first fraction obtained in the experiment was recrystallised, and then treated in the same manner with alcoholic potash, and a small quantity of pilocarpine nitrate (m. p. 176°) isolated from the resulting product.

It was therefore absolutely proved that pure *iso*pilocarpine nitrate, like pilocarpine nitrate, is converted by the action of alcoholic potash into an equilibrium mixture consisting chiefly of *iso*pilocarpine with a small percentage of pilocarpine. This experiment therefore affords further evidence that pilocarpine and *iso*pilocarpine are not structural isomerides but stereoisomerides.

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LXXXI.—*The Chlorination of Methyl Derivatives of Pyridine. Part I. 2-Methylpyridine.*

By WILLIAM JAMES SELL, M.A., F.R.S.

FEW changes among analogues show a greater difference and exemplify better the influence of the nitrogen atom than the direct action of chlorine on benzene and toluene as contrasted with its effect on pyridine and picoline. In the former series, as is well known, no great difficulty is experienced in obtaining fairly regular chlorination and good yields, whilst in the latter the molecule for the most part breaks down and the products form a tar-like mass, from which mere traces of a mixture of chlorinated derivatives can be isolated. Moreover, 2-methylpyridine, unlike pyridine, blackens at once when heated with phosphorus pentachloride either with or without phosphorus oxychloride, and further experiments with this reagent were abandoned.

In these circumstances, recourse was had to the process found successful in the case of pyridine (Trans., 1899, **75**, 979), namely, the direct chlorination of 2-methylpyridine hydrochloride saturated with hydrochloric acid, the product thus formed remaining liquid at the ordinary temperature of the laboratory. According to Ramsay (*Phil. Mag.*, 1876, II, [iv], 2), "picoline hydrochloride is not acted on by chlorine even when heated with it," but whilst this statement was found to be true at the ordinary temperature, it ceases to be so as the temperature rises, and at 105—110° the hydrogen is rapidly replaced without darkening and substitution derivatives are readily produced. How far this difference is due to the fact that in the work here recorded the 2-methylpyridine hydrochloride was saturated with hydrochloric acid remains to be seen.

It is hoped that conditions may be found under which the hydrogen of the side-chain and nucleus may be separately replaced, but so far the experiments have in the main been confined to the study of a more complete displacement in which both the hydrogen of the methyl group and the nucleus has been involved. So far, the only solid substance isolated as the result of the chlorination is hexachloropicoline, melting at 102—103°, the composition of which is represented by the formula C_6HCl_6N. This compound readily yields successively trichloropicolinic acid and trichloropyridine. The hexachloropicoline is isomeric with the substance (m. p. 60°) obtained by Ost (*J. pr. Chem.*, 1893, [ii], **27**, 257) by the action of phosphorus pentachloride on comenamic acid. In addition to the foregoing compound, there is a liquid product consisting of less highly chlorinated compounds, the work on which, although

advanced, is still incomplete and will form the subject of a further communication.

It is worthy of remark that there is a total absence of the dipyridyl derivative, of which such a large quantity was produced in the chlorination of pyridine hydrochloride (Trans., 1899, **75**, 979; 1901, **79**, 899). This, of course, was expected, seeing that the 2-position—to which the second pyridine nucleus is attached—is in this instance occupied by the methyl group. The solid compound (m. p. 102—103°) already mentioned, when gently heated with approximately eighty per cent. sulphuric acid, gives a nearly quantitative yield of trichloropicolinic acid, $C_5HNCl_3{\cdot}CO_2H$, showing that three of the six atoms of chlorine in the original compound belong to the side-chain. This trichloropicolinic acid, when distilled with glycerol, breaks down giving a quantitative yield of a trichloropyridine (m. p. 72—73°) identical with the compound erroneously described by Keiser (*Amer. Chem. J.*, 1886, **8**, 310) as the hydrochloride of a dichloropyridine and subsequently proved by Sell and Dootson (Trans., 1898, **73**, 442) to be a trichloropyridine. This substance is produced, not only by the direct chlorination of pyridine, but also by the action of phosphorus pentachloride on that substance (Sell and Dootson, Trans., 1898, **73**, 437). From the general properties and particularly the highly basic character of this trichloropyridine, it was suspected that the chlorine atoms occupied the positions 3, 4, and 5, and the experimental verification of this assumption should be possible when based on the following considerations.

We may take for comparison the substance 3 : 4 : 5-trichloro-2-aminopyridine, the formula of which may be thus depicted:

```
       Cl
   Cl/  \Cl
     |   |
   H\  /NH2 .
      N
```

This compound, the preparation and orientation of which were described by Sell and Dootson (Trans., 1899, **75**, 980; 1900, **77**, 771), should also be obtainable from the trichloropicolinic acid mentioned above by converting it into its amide, and the latter by the Hofmann reaction into the foregoing 3 : 4 : 5-trichloro-2-aminopyridine. The reactions were carried out and resulted in a substance indistinguishable from, and therefore identical with, the compound having the above graphic formula. It may therefore be definitely concluded that in the compounds here described the chlorine atoms in the nucleus occupy the positions 3, 4, and 5, and that in compound I the hydrogen of the methyl group is entirely replaced by chlorine:

I.		II.	III.
2,3,5-trichloro ring: Cl, Cl, Cl, H, CCl_3, N	→	Cl, Cl, Cl, H, CO_2H, N	Cl, Cl, Cl, H, H, N

Experimental.

The 2-methylpyridine used in this work was in the main obtained from Schuchardt, and was subsequently carefully purified by means of its mercurichloride, a process involving much time and labour. The base was recovered from the double salt (m. p. 154°) by caustic soda, and fractionated after drying over caustic potash. Another specimen of the base was purchased from Kahlbaum.

The hydrochloride was made by saturating the 2-methylpyridine with hydrogen chloride, in which process it absorbs nearly double the theoretical amount of the gas and gives an oily liquid with no tendency to crystallise at the ordinary temperature of the laboratory.

After preliminary trials of small quantities of the hydrochloride under various conditions, it was found that chlorine had no action at the ordinary temperature either in the dark or in bright sunshine, or even in presence of such chlorine carriers as iodine or ferric chloride. When, however, the temperature of the hydrochloride was raised to 100°, fumes of hydrogen chloride were abundantly formed, and the flask containing the substance rapidly increased in weight. In the early stages of the work, several portions were chlorinated at 100°, but it was subsequently found that at 105—110° the absorption of chlorine was still more rapid, and the later experiments were carried out at this temperature.

As the chlorination proceeded, as in the similar work with pyridine hydrochloride, a heavy layer was formed in the liquid which increased in quantity until finally the upper layer disappeared and no increase in weight occurred. During the chlorination, the tube conveying the chlorine was kept as much as possible in the upper layer. The product was cooled by ice and a slow current of air aspirated through for several hours to remove free chlorine, during which operation a copious white, crystalline deposit separated. This was filtered off, and after thorough draining from the liquid product crystallised from alcohol. The crystals are prismatic in form, and dissolve in alcohol and most organic solvents but are insoluble in water. The substance melts at 102—103° without decomposition. The average yield of the recrystallised substance was over 52 per cent. of the 2-methylpyridine taken.

0·2500 gave 0·2195 CO_2 and 0·0116 H_2O. C = 23·94; H = 0·51.
0·2195 ,, 0·630 AgCl. Cl = 71·0.
C_6HNCl_6 requires C = 24·00; H = 0·33; Cl = 71·0 per cent.

Conversion of Hexachloropicoline into 3 : 4 : 5-*Trichloropicolinic Acid.*

After preliminary trials, fifty grams of the preceding compound were dissolved in 150 c.c. of 80 per cent. sulphuric acid and heated at 120—130° in a reflux apparatus for from 1½—2 hours, the heating being discontinued when fumes of hydrogen chloride ceased. If the temperature is allowed to rise much higher than 130°, a good deal of the trichloropicolinic acid is decomposed into trichloropyridine, which remains in solution in sulphuric acid. When the temperature of the mixture is carefully kept within the above limit, a nearly theoretical yield of the acid is obtained by pouring the mixture into water, collecting the precipitated acid, and recrystallising from boiling water or alcohol. The substance separates from these menstrua in small, white, anhydrous, short, pointed needles or in filamentous rosettes of needles, according to the temperature of deposition; it melts at 164—165° (uncorr.) with effervescence. The compound dissolves to a moderate extent in boiling, and very sparingly in cold, water and in acetic acid; it is fairly soluble in boiling alcohol and in most organic solvents.

0·2038 gave 0·388 AgCl. Cl = 47·09.
$C_5HNCl_3 \cdot CO_2H$ requires Cl = 47·02 per cent.

A solution of the acid gives the following reactions:

(1) With silver nitrate, a white, gelatinous silver salt which is sparingly soluble in boiling water, from which it separates in filamentous needles.

(2) When a soluble copper salt is added to a hot solution of the acid, a light blue, crystalline (apparently rhombohedral) precipitate of the copper salt is produced, which is very sparingly soluble in either hot or cold water.

(3) Ferrous sulphate produces at first a yellowish-brown colour, but after a short time the solution deposits microscopic rosettes of dark red prisms.

(4) The lead and mercuric salts separate in the form of white rosettes of very sparingly soluble needles or prisms.

Formation of 3 : 4 : 5-*Trichloropyridine from* 3 : 4 : 5-*Trichloropicolinic Acid.*

A sample of the pure acid weighing five grams was mixed with 20 c.c. of glycerol, and the mixture rapidly distilled from a small retort until nothing more in the nature of an oil was visible in the

flask used as a condenser. The oily portion of the distillate solidified in the flask to a crystalline mass which, when washed and dried, weighed 3·9 grams, the calculated yield being 4·02 grams. The substance separates from solution in hot alcohol in long, colourless needles melting at 72—73° (uncorr.). The melting point here given is 1° higher than that recorded by Keiser (*Amer. Chem. J.*, 1886, 8, 310) and by Sell and Dootson (Trans., 1898, 73, 438), and is not materially affected when the compound is mixed with samples from different sources.

0·1736 gave 0·411 AgCl. Cl = 58·5.
C_5HNCl_3 requires Cl = 58·4 per cent.

The compound from other sources, as shown (*loc. cit.*), gives a platinum salt having the formula $(C_6H_2Cl_3N)_2PtCl_4$, containing 27·66 per cent. of platinum. A specimen prepared from the trichloropyridine from trichloropicolinic acid furnished the following numbers:

0·1635 gave 0·0445 Pt. Pt = 27·21 per cent.

As a further confirmation, samples of the double salt with mercuric chloride from the different sources were compared, and found to be practically identical in melting point and general characters.

Formation of Methyl 3 : 4 : 5-*Trichloropicolinate.*

Methyl 3 : 4 : 5-trichloropicolinate was prepared by saturating a mixture of the acid and methyl alcohol with hydrogen chloride. On leading the gas into the cold mixture, the acid gradually dissolved, and on passing in a further quantity of this reagent a crystalline precipitate of the ester separated. This was removed by filtration and more gas passed into the filtrate until complete saturation was effected. After standing for twelve hours, the excess of hydrogen chloride was removed by a current of dry air, and the excess of alcohol by distillation in a partial vacuum. The deposited ester was recrystallised from methyl alcohol, from which it separates in colourless plates, having a pearly lustre and melting at 84—85° (uncorr.). The ester is freely soluble in organic solvents and moderately so in boiling water, from which it separates in plates, the melting point being unaltered.

Formation of 3 : 4 : 5-*Trichloropicolinamide from Methyl* 3 : 4 : 5-*Trichloropicolinate.*

When the methyl ester was dissolved in hot methyl alcohol and an excess of strong aqueous ammonia added, the amide rapidly separated as a crystalline magma of fine needles; this substance, when collected and recrystallised from spirit, formed long, colourless, flat needles

melting at 184—185° (uncorr.); it is freely soluble in most organic solvents, and moderately so in boiling water, from which it separates on cooling (184—185°, uncorr.).

0·1860 gave 0·3529 AgCl. Cl = 47·02.
0·2445 „ 0·4628 „ Cl = 46·86.
$C_5HNCl_3 \cdot CONH_2$ requires Cl = 47·22 per cent.

Formation of 3 : 4 : 5-*Trichloro-2-aminopyridine from* 3 : 4 : 5-*Trichloropicolinamide.*

The Hofmann reaction was carried out on 4·5 grams of the picolinamide, using the theoretical amounts of bromine and caustic potash. The only deviation from the usual procedure was the filtration of the crystalline compound from the cooled alkaline solution and its purification by distillation in a current of steam, to avoid the risk of any possible decomposition by distillation from the strongly alkaline liquid. All but mere traces of the crystalline product came over during the steam-distillation, and when collected and recrystallised from alcohol formed a mass of fine needles melting at 160—161° (uncorr.).

0·2870 gave 35 c.c. nitrogen at 24° and 767 mm. N = 13·78.
Trichloroaminopyridine, $C_5H_2N_2Cl_3$, requires N = 14·17 per cent.
Trichloropicolinamide, $C_5HNCl_3CONH_2$, requires N = 12·41 per cent.

In conclusion, the author desires gratefully to acknowledge his indebtedness to the Government Grant Committee of the Royal Society for providing the greater part of the funds requisite for this research.

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LXXXII.—*Further Studies on Dihydroxymaleic Acid.*

By Henry John Horstman Fenton, M.A., F.R.S.

The mode of formation, constitution, properties and relationships of dihydroxymaleic acid have been discussed in several previous communications to the Society and elsewhere (Trans., 1894, **65**, 899; 1895, **67**, 48 and 774; 1896, **69**, 546; 1897, **71**, 375; 1898, **73**, 71; 1902, **81**, 426; Proc., 1898, **14**, 119; *Proc. Camb. Phil. Soc.*, 1901, **11**, 109; 1902, **11**, 358, &c.), and in the present paper an account is given

of some of the principal investigations which have since been carried out in connection with the subject.

This acid proves to be of importance not only in consequence of the scientific interest attaching to its constitution and peculiar mode of formation, but also because it serves as the starting point for the preparation, by direct and simple transformations, of many compounds which can otherwise only be obtained with considerable difficulty or not at all.

In the communications above referred to it was shown that the acid results from the oxidation of tartaric acid in presence of ferrous iron; it is thus obtained in the form of lustrous, diamond-shaped plates which have the formula $C_4H_4O_6,2H_2O$. It is a dibasic acid, as evidenced by the composition of its salts and esters; the presence also of two alcoholic hydroxyl groups is shown by the action of acetic anhydride and of acetyl and benzoyl chlorides. In constitution it must therefore be represented as either dihydroxymaleic or dihydroxyfumaric acid, $CO_2H{\cdot}C(OH){:}C(OH){\cdot}CO_2H$. The former configuration is to be preferred in consequence of the readiness with which anhydride formation takes place, and the action of hydrobromic acid transforms it into an isomeric modification which has probably therefore the fumaroid form; it cannot be said, however, that these respective configurations are finally established (compare Proc., *loc. cit.*).

Fuming hydriodic acid reduces it ultimately to succinic acid, racemic acid having been isolated as an intermediate stage. When oxidised by bromine under certain conditions, it is converted almost quantitatively to dihydroxytartaric acid; this action was shown to be reversible and, under different conditions, bromine is liberated when hydrogen bromide acts on dihydroxytartaric acid with the production of the lactonic acid of dihydroxyfumaric acid. By heating an aqueous solution of dihydroxytartaric acid, tartronic acid is obtained in a pure condition.

Oxidation by means of ferric salts converts dihydroxymaleic acid into the semialdehyde of mesoxalic acid, and it was pointed out that the latter product also results when tartaric acid is oxidised by chlorine in presence of iron.

An aqueous solution of dihydroxymaleic acid, when heated to about 50—60°, gives off carbon dioxide and yields glycollic aldehyde; by distillation of the resulting solution under reduced pressure, the latter compound is obtained in a crystalline condition.

The methyl and ethyl esters are crystalline solids, and it was shown that the former exists in two modifications; later investigation indicates that the ethyl ester behaves similarly, but the two forms have not yet been completely examined.

Notwithstanding the conclusive evidence above referred to in

support of the dihydroxy-formula for this acid, it is not improbable, as was previously suggested (Trans., 1896, 69, 547), that the compound may, under certain conditions, assume the tautomeric keto-form,

$$CO_2H\cdot CO\cdot CH(OH)\cdot CO_2H,$$

and in some of the later observations it will be noticed that the latter constitution suggests the more rational interpretation of the changes involved.

Condensation with Ammonia. Synthesis of Pyrazinedicarboxylic Acid.

When the ammonium or the sodium salt of dihydroxymaleic acid is mixed with an excess of strong aqueous ammonia and the mixture is allowed to stand for some days at the ordinary temperature, the salt slowly dissolves, and the solution acquires a bright yellow colour. This change is greatly accelerated if the mixture is warmed on a water-bath at about 50—60°, and appears under these conditions to be completed in about half an hour. After removal of the excess of ammonia by evaporation or by distillation under reduced pressure, the addition of an acid causes the evolution of much carbon dioxide together with the separation of a brown, crystalline precipitate consisting of small, transparent prisms. These are very sparingly soluble in boiling water, alcohol, or other solvents, but dissolve easily in alkalis. They dissolve also in concentrated sulphuric acid, and separate out on dilution with water. By repeated recrystallisation from boiling aqueous alcohol or by solution in dilute alkalis and reprecipitation with acids, the crystals become practically colourless. The yield of this product is not large, but it appears to be increased if a current of air is drawn through the mixture during the preparation; in this case also the resulting crystals are less discoloured.

The aqueous solution of this substance is acid towards indicators and effervesces with sodium carbonate; with ferrous sulphate, it develops a beautiful violet colour, which is discharged by mineral acids or by alkalis. Ferric salts, on the other hand, produce no colour. Silver, lead, barium, and calcium salts give white precipitates from which the acid can be regenerated in the usual ways; the calcium salt separates from hot solutions in prisms. The solid acid, when heated, begins to decompose, and partly vaporises between 250° and 300° without melting.

Analysis of the purified crystals when dried in a vacuum desiccator gave the following results:

0·1529 gave 0 2397 CO_2 and 0·0372 H_2O. C = 42·75; H = 2·70.
0·2861 ,, 40·6 c.c. nitrogen at 18° and 748 mm. N = 16·43.
$C_3H_2NO_2$ requires C = 42·85; H = 2·38; N = 16·66 per cent.

0·1291 of the air-dried crystals, when kept in a vacuum desiccator until the weight was constant, lost $H_2O = 0·0226$; $H_2O = 17·50$.

$C_3H_2NO_2,H_2O$ requires $H_2O = 17·64$ per cent.

0·3322 of the vacuum-dried crystals, when dissolved in standard caustic soda and titrated with standard sulphuric acid, required 7·1 c.c. of caustic soda solution containing 22·386 NaOH per litre. An acid having the formula $(C_3H_2NO_2)_n$, if *n*-basic, would require 7·06 c.c.

From the above results, it is evident that the composition and properties of this acid correspond in every respect with those of the *pyrazine*-2 : 5-*dicarboxylic acid*, $C_4H_2N_2(CO_2H)_2,2H_2O$, which was first obtained by Stoehr (*Ber.*, 1891, **24**, 4105) by the oxidation of dimethylpyrazine with potassium permanganate.

The same acid was prepared by Wolff (*Ber.*, 1893, **26**, 721) in the following way. β-Hydroxy-(or β-bromo-)lævulic acid condenses with ammonia to give tetramethylpyrazine, $2C_5H_8O_4 + 2NH_3 = C_4N_2(CH_3)_4 + 2CO_2 + 4H_2O + H_2$, and by oxidation of the latter with potassium permanganate the somewhat unstable tetracarboxylic acid, $C_4N_2(CO_2H)_4$, is obtained. The dipotassium salt of this, when heated with water to about 200°, yields the dicarboxylic acid, together with pyrazine and other products.

The identity of the product obtained in the present instance with this dicarboxylic acid is further confirmed by its behaviour when heated. The vacuum-dried substance, when heated in a small distilling flask to about 280—300°, gave a white, solid sublimate, together with a volatile liquid which solidified in the neck of the flask to a crystalline mass. These crystals melted at 55°, had the characteristic heliotrope odour of pyrazine, and their aqueous solution gave, with mercuric chloride, a white precipitate.

In the condensation of hydroxylævulic acid with ammonia, as in the formation of dimethylpyrazine from aminoacetone by heat (Gabriel and Pinkus, *Ber.*, 1893, **26**, 2205) and of pyrazine from aminoacetaldehyde or aminoacetal (Wolff, *loc. cit.*, 1830), it will be observed that the changes involved imply the loss of two atoms of hydrogen; for this reason, the addition of oxidising agents, such as mercuric chloride, improves the yield. In the present case, the condensation is of the same type, $2C_4H_4O_6 + 2NH_3 = C_4H_2N_2(CO_2H)_2 + 4H_2O + 2CO_2 + H_2$, but it has not so far been found advantageous to employ oxidising agents other than air, since the addition of metallic salts, such as mercuric chloride, leads to undesirable complications.

With regard to the mechanism of the change, there are, of course, several possible explanations. If carbon dioxide is eliminated in the first stage, the initial product may be tartronic semialdehyde,

$$CHO·CH(OH)·CO_2H,$$

hydroxypyruvic acid, $CH_2(OH)\cdot CO\cdot CO_2H$, or dihydroxyacrylic acid, $CH(OH){:}C(OH)\cdot CO_2H$; condensation of any of these acids with ammonia would evidently take place in a manner similar to that in which Wolff (*loc. cit.*) represents the formation of pyrazine from aminoacetaldehyde. From tartronic semialdehyde, for example, the changes might be as follows

$$\begin{array}{ccc} NH_2 & & \\ CO_2H\cdot CH & CHO & \\ CHO & HC\cdot CO_2H & \\ & NH_2 & \end{array} \rightarrow \begin{array}{cc} & NH \\ CO_2H\cdot CH & HC\cdot OH \\ OH\cdot CH & HC\cdot CO_2H \\ & NH \end{array} \rightarrow$$

$$\begin{array}{cc} & N \\ CO_2H\cdot C & CH \\ HC & C\cdot CO_2H \\ & N \end{array} + 2H_2O + H_2.$$

On the other hand, the initial product may be a tetracarboxylic acid which, by oxidation and loss of carbon dioxide, gives the dicarboxylic acid in question :

$$\begin{array}{c} CO_2H\cdot C\cdot OH \\ CO_2H\cdot C\cdot OH \end{array} + 2NH_3 + \begin{array}{c} OH\cdot C\cdot CO_2H \\ OH\cdot C\cdot CO_2H \end{array} \rightarrow \begin{array}{cc} & NH \\ CO_2H\cdot C & C\cdot CO_2H \\ CO_2H\cdot C & C\cdot CO_2H \\ & NH \end{array}.$$

A change of an entirely different character takes place when the ethyl or methyl ester of dihydroxymaleic acid is treated with aqueous ammonia.

In this case the liquid assumes a deep orange-red colour, and a white precipitate separates which proves to be *oxamide*. The solution contains ammonium oxamate together with another substance which has not yet been obtained sufficiently pure for analysis. It is evident, therefore, that disruption occurs, under these conditions, at the double linkage.

Action of Hydrazines.

It was previously shown (Trans., 1896, 69, 548) that dihydroxymaleic acid reacts with phenylhydrazine only to produce a *salt*, $C_4H_4O_6,2N_2H_3\cdot C_6H_5$, a brilliant silver-white, crystalline substance which, when heated for some time with phenylhydrazine acetate solution, becomes orange-yellow, loses carbon dioxide, and is converted into Nastvogel's osazone of glyoxalcarboxylic acid :

$$CH{:}N_2HPh\cdot C{:}N_2HPh\cdot CO_2H;$$

this crystallises in needles or prisms which melt at 222—224° (compare Trans., 1901, **79**, 100, and 1902, **81**, 430).

When the salt is boiled with water alone, it behaves similarly, but in this case the osazone remains principally dissolved as a colloidal solution, from which it immediately separates on the addition of a drop of acetic acid.*

Other hydrazines are now found to behave with dihydroxymaleic acid in a similar way; hydrazine hydrate, for example, gives a white precipitate consisting of long needles or prisms, which has the composition $C_4H_4O_6,2N_2H_4$. Analysis gave N = 26·55 per cent., theory requiring 26·41 per cent.

Phenylbenzylhydrazine likewise gives a white, flocculent precipitate which, when washed with alcohol and dried in a vacuum desiccator, melts at 128—130°, and gives, on analysis, N = 10·57 per cent., $C_4H_4O_6 \cdot 2N_2H_2BzPh$ requiring 10·29 per cent. When this salt is heated with water to boiling for about an hour, it becomes converted into a gummy mass, which, when treated with hot alcohol, only partially dissolves. The residue, after treatment with alcohol, was recrystallised first from hot benzene and then from a mixture of toluene and absolute alcohol; in this way, it was obtained in the form of nearly colourless prisms which are aggregated together, and which, when exposed to the air, gradually turn pink at the edges. These crystals, after drying at 100°, melted at 197°.

0·1590 gave 0·4680 CO_2 and 0·0905 H_2O. C = 80·27; H = 6·32.
0·1445 „ 17·27 c.c. nitrogen at 19·5° and 731 mm. N = 13·46.
$C_{28}H_{26}N_4$ requires C = 80·38; H = 6·22; N = 13·39 per cent.

This product is therefore evidently the phenylbenzylosazone of glyoxal,† $\begin{array}{l}CH{:}N_2BzPh\\ |\\ CH{:}N_2BzPh\end{array}$, which was first obtained by Ruff and Ollendorff from the products resulting when galactonic and lactobionic acids are oxidised in presence of iron; it was also obtained by the same authors directly from glyoxal (*Ber.*, 1900, **23**, 1806).

When glycollic aldehyde is heated for some time on a water-bath with an alcoholic solution of phenylbenzylhydrazine, a product is obtained which is in all respects the same as the osazone here described. It is evident that in this case the $CH_2 \cdot OH$ group becomes oxidised, that is to say, that an osazone is formed from a sugar of the aldose type

* When the phenylhydrazine salt is heated with dry pyridine the product consists principally of the phenylosazone of glyoxal.

† Strictly speaking, this is of course a *dihydrazone* of glyoxal or an *osazone* of glycollic aldehyde, but the above name is employed in accordance with common usage.

by the action of a secondary aromatic hydrazine (compare Ofner, *Ber.*, 1904, **37**, 3362).

It was previously stated that methyl and ethyl dihydroxymaleates give no reaction with phenylhydrazine; this is true as regards the initial result, but it is now found that on prolonged heating a change does slowly take place. When, for example, the ethyl ester is heated on a water-bath with phenylhydrazine acetate in either alcoholic or acetic acid solution for about an hour and is then allowed to stand for some time, an orange-coloured precipitate slowly separates. This, after being washed with cold alcohol and recrystallised from hot alcohol or glacial acetic acid, is obtained in the form of brilliant orange-coloured prisms which melt sharply at 154°. On analysis, these gave C = 63·57, H = 4·79 per cent., the formula $C_{18}H_{16}O_3N_4$ requiring C = 64·28, H = 4·76. The properties of this compound correspond in every way with those of the product which Wislicenus and Scheidt (*Ber.*, 1891, **24**, 4210) obtained by the action of phenylhydrazine on the ethyl ester of ethoxyoxaloacetic acid, and which they designate as the ethyl ester of phenylhydrazoneketophenylpyrazolonecarboxylic acid,

$$NPh\begin{matrix} \diagup N{=}C\cdot CO_2Et \\ \diagdown CO\cdot C{:}N_2HPh \end{matrix}.$$

The same compound was obtained by Anschütz and Parlato by the action of phenylhydrazine on the ethyl ester of dioxosuccinic acid (*Ber.*, 1892, **25**, 1979), and it results also from either of the three isomeric osazones of ethyl dioxosuccinate when they are heated with glacial acetic acid (Anschütz and Pauly, *Ber.*, 1895, **28**, 66).

When ethyl dihydroxymaleate is heated with an excess of phenylhydrazine in alcoholic solution, there is also formed after a time a bright scarlet substance, which is nearly insoluble in boiling alcohol and which melts at 256—259°. This is evidently the compound first noticed by Peny, which arises from the action of phenylhydrazine on either the ethyl or propyl esters of dioxosuccinic acid (*loc. cit.*, 67).

It appears therefore that the final products obtained by the continued action of phenylhydrazine on the esters of dihydroxymaleic acid are the same as those which result from dioxosuccinic esters,

$$CO_2R\cdot CO\cdot CO\cdot CO_2R,$$

that is, the esters obtained from dihydroxytartaric acid.

The above results are most easily interpreted if it is supposed that dihydroxymaleic acid assumes the tautomeric form

$$CO_2H\cdot CO\cdot CH(OH)\cdot CO_2H,$$

and that the CHOH group is oxidised by phenylhydrazine in the usual way.

Preparation of the Acid (compare Trans., 1894, **65**, 901).

A cold, nearly saturated solution of tartaric acid, containing a small proportion of iron in the ferrous condition, is surrounded by a freezing mixture, and a previously cooled solution of hydrogen peroxide (20 volume or stronger) is very slowly added, in small portions at a time, with constant stirring, until the mixture assumes a nearly permanent black tint.

No separation of the acid occurs from this mixture even on long standing, unless a dehydrating agent is added. Nordhausen sulphuric acid was found to be the most suitable agent for this purpose; it has, of course, to be introduced with the greatest care in order to prevent rise of temperature, and is best dropped from a long funnel below the surface of the liquid. After persistent stirring, the crystals of dihydroxymaleic acid begin to separate in a few minutes and continue to deposit for several days when the mixture is kept at about 0°.

The yield of the product is always small as compared with the amount of tartaric acid employed: this is partly due to the unstable nature of the acid and to the fact that a considerable portion remains in solution after crystallisation ceases; but the principal cause is to be found in the circumstance that the product itself is very readily oxidised by hydrogen peroxide in presence of iron (compare Fenton and Ryffel, Trans., 1902, **81**, 434), and the oxidising agent only preferentially attacks the tartaric acid when the latter is in large excess. For this reason, it is never advantageous to employ more than about one-tenth of the calculated quantity of hydrogen peroxide.

Many experiments have been undertaken with the object of improving the yield, but so far only with partial success. The substitution of orthophosphoric acid (sp. gr. 1·7) for Nordhausen sulphuric acid as a dehydrating agent is found to be an advantage in many respects; the yield certainly appears to be better and the reagent may be added with greater boldness and with less danger of a rise in temperature, but it is important to make sure of the absence of impurities, such as sodium or calcium salts, which would contaminate the product.

When anhydrous sodium sulphate is used in place of the above-named dehydrating agents, the product which separates proves to be the *acid sodium* salt; the yield of this is very much greater, in proportion to theory, than that of the free acid when acid dehydrators are used, and for certain purposes the manufacture of this salt is therefore to be preferred.

Acid Sodium Salt.

If to the mixture obtained by oxidation of tartaric acid in the manner above described a strong solution of a sodium salt is added, a bulky, crystalline precipitate soon separates, which consists of long, lustrous needles or prisms; addition of the sodium salt in the solid state gives a similar result. This product is less soluble than sodium hydrogen tartrate, and it is advisable, if the solid salt is used, so to adjust the final concentration of the mixture (by previous trial with a small portion of the original solution) that no separation of the acid tartrate is likely to occur.

This product, dried in the air, was analysed with the following results:

I. 0·5086 gave 0·1736 Na_2SO_4. Na = 11·05.
II. 0·3107 ,, 0·1072 Na_2SO_4. Na = 11·19.
$NaHC_4H_2O_6,2H_2O$ requires Na = 11·16 per cent.

The aqueous solution of this salt has a strongly acid reaction, and when titrated with caustic soda, using phenolphthalein as indicator, the following numbers were obtained:

III. 1·0953 grams required 8·7 c.c. soda solution, containing 14·13 grams Na per litre, theory requiring 8·6 c.c.

This salt is more stable than the free acid and may be recrystallised from hot water with but little loss; when, however, the aqueous solution is heated for some time, or when it is boiled, carbon dioxide is evolved and a white precipitate separates; the solution remaining gives the reactions of glycollic aldehyde, and the white precipitate proves to be the normal salt of dihydroxymaleic acid. 0·1855 gave 0·1344 Na_2SO_4. Na = 23·47. $Na_2C_4H_2O_6$ requiring Na = 23·95 per cent.

It is evident, therefore, that the acid salt breaks up into normal salt and free acid, the latter then yielding glycollic aldehyde and carbon dioxide.

When this acid salt is covered with acetic acid and treated with bromine in slight excess, it is, like the free acid, oxidised to the state of dihydroxytartrate, the change being approximately quantitative:—

2·9 grams of acid sodium dihydroxymaleate, when oxidised by bromine and the product neutralised with sodium carbonate, gave 3·7 grams of sodium dihydroxytartrate (air-dried), the theoretical amount being 3·81.

Oxidation with Mercuric Oxide. Preparation of Mesoxalic Acid.

When dihydroxymaleic acid is shaken with cold water and the calculated quantity of freshly precipitated mercuric oxide, it is gradually oxidised to dihydroxytartaric acid with separation of metallic mercury. Further, when an aqueous solution of dihydroxytartaric acid is heated at about 50—60° with mercuric oxide in calculated quantity, carbon dioxide is evolved and the solution contains mesoxalic acid. The solution so obtained is free from mercury, but is liable to contain some oxalic acid, especially if the temperature is not carefully regulated. The operation may, of course, be performed in a single stage from dihydroxymaleic acid, using two molecules of mercuric oxide for one molecule of the acid.

For the purpose of obtaining pure mesoxalic acid, however, it is found preferable to start with dihydroxytartaric acid, prepared in the manner previously described (Trans., 1898, **73**, 72), and to employ an excess of mercuric oxide.

In this case, mesoxalic acid is converted into a sparingly soluble mercury salt, and by decomposing this with hydrogen sulphide, avoiding excess, the acid is obtained free from oxalic acid. On evaporation of the resulting solution in a vacuum desiccator over sulphuric acid, deliquescent crystals of mesoxalic acid remain, which are practically pure without recrystallisation, the product melting at about 110—115°.

On addition of phenylhydrazine hydrochloride or acetate to the aqueous solution, the pale yellow needles of mesoxalic acid phenylhydrazone begin, after a few minutes, to separate in the cold. These, after being well washed and dried in a vacuum desiccator, melted at 170—171° (compare Trans., 1902, **81**, 433).

0·1498 gave 17·5 c.c. nitrogen at 18° and 759 mm. N = 13·73.

$C_9H_8O_4N_2$ requires N = 13·46 per cent.

It would appear that this reaction affords one of the most simple methods for the preparation of mesoxalic acid, and the yield is good; from one gram of dihydroxytartaric acid, 1·1 grams of mesoxalic acid hydrazone were obtained, the theoretical yield being about 1·2 grams.

Formation of Mesoxalic Semialdehyde.

It was shown in a former communication (Fenton and Ryffel, Trans., 1902, **81**, 434) that when dihydroxymaleic acid reacts with ferric salts in aqueous solution at about 40°, carbon dioxide is liberated, and the resulting solution contains the semialdehyde of mesoxalic acid, $CHO·CO·CO_2H$. This product was identified by (*a*) the immediate

formation of Nastvogel's osazone when the solution is mixed with phenylhydrazine acetate, (*b*) the oxidation to mesoxalic acid by means of alkaline cupric hydroxide, and (*c*) the production of Söderbaum's dioximinopropionic acid by the action of hydroxylamine.

An objection to this mode of preparation of the semialdehyde is the difficulty of removing the large amount of ferrous salt which is produced in the reaction. Later investigation has shown that mercuric chloride may advantageously be employed as oxidising agent and that the mercury is, in this case, entirely separated as calomel, according to the relation

$$C_4H_4O_6 + 2HgCl_2 = C_3H_2O_4 + 2HgCl + 2HCl + CO_2.$$

The mercuric chloride is dissolved in hot water and the solution kept at about 60—70°; the calculated quantity of crystallised dihydroxymaleic acid is added in small portions at a time, and the mixture is then allowed to stand for an hour or two. The resulting solution, if the proportions have been accurately adjusted, is now practically free from mercury, any traces which may remain being removed by cautious addition of hydrogen sulphide. The solution gives all the reactions of mesoxalic semialdehyde, and it may be obtained free from the admixed hydrochloric acid by careful addition of the calculated quantity of silver carbonate; the product, however, appears to be much more stable in presence of free hydrochloric acid, and in this condition it may be preserved for some time with but little change. It may be evaporated to the consistence of a syrup in a vacuum desiccator, over solid caustic potash and sulphuric acid, and even rapid evaporation on a water-bath does not altogether destroy it; but when the solution is boiled for some time or is repeatedly evaporated it loses carbon dioxide yielding glyoxal. These changes can be easily followed by examination of the osazones resulting from the addition of phenylhydrazine.

Mesoxalic semialdehyde is not destroyed by neutralisation with sodium carbonate in the cold; boiling with sodium carbonate, however, changes it to tartronic acid (see below).

Since the aldehyde-hydrate of mesoxalic semialdehyde,

$$CH(OH)_2\cdot CO\cdot CO_2H,$$

might be tautomeric with the missing trihydroxyacrylic acid,

$$C(OH)_2{:}C(OH)\cdot CO_2H,$$

it appeared to be possible that the substance should, under certain conditions, condense with urea to give uric acid, and several experiments are being made in this direction. When the aqueous solution of the semialdehyde is mixed with urea and allowed to stand for several hours, a crystalline substance slowly separates; the change is

accelerated when hydrochloric acid is present, and it takes place in a few minutes if the mixture is heated on a water-bath.

This crystalline product is very sparingly soluble in boiling water, but dissolves easily in alkalis ; it dissolves also in cold concentrated mineral acids, and separates again in the crystalline form when the solutions are diluted with water. The crystals consist either of needles, prisms, or octahedra according to the conditions under which they are separated ; they are at first somewhat discoloured, but by repeated recrystallisation become quite colourless.

When heated, the substance decomposes without melting, giving off hydrogen cyanide, ammonia, and a white sublimate. So far many of the properties resemble uric acid, but when evaporated with nitric acid the white or yellow residue obtained gives only a brownish-orange colour on addition of ammonia. If strong nitric acid is used in this experiment and the residue, after evaporation, is treated with caustic potash or soda, a faint bluish-violet colour is produced, and this, on the addition of a drop of sodium hypochlorite, changes to an intense purple coloration.

Analysis of the crystals, dried at 100°, furnished the following results :

0·1133 gave 0·1378 CO_2 and 0·0435 H_2O. C = 33·17 ; H = 4·26.
0·0859 „ 28·9 c.c. nitrogen at 19° and 755 mm. N = 39·19.
($C_2H_3ON_2$) requires C = 33·80 ; H = 4·22 ; N = 39·43 per cent.

From the above results it is evident that the product is *glycoluril*,

$$CO\left\langle\begin{matrix}NH\cdot\overset{H}{C}\cdot NH\\ NH\cdot\underset{H}{C}\cdot NH\end{matrix}\right\rangle CO,$$

or "acetylene-urea," which was first obtained by Reineck (*Annalen*, 1864, **131**, 119) by the reduction of allantoin with sodium amalgam ; Schiff obtained the same substance later (*Annalen*, 1877, **189**, 157) by the condensation of urea with glyoxal, and the products derived from these two sources were at first thought to be different. Widmann, however (*Ber.*, 1886, **19**, 2477), carefully compared the properties of the products and showed that they were identical.

The properties of glycoluril, as described by these authors, coincide entirely with those of the substance at present under consideration, but the remarkable colour reaction given by alkaline hypochlorites in the manner above-mentioned appears to have been entirely overlooked.

The formation of glycoluril in the present case may, of course, arise from the action of urea on glyoxal, supposing that the latter is first

formed by decomposition of the mesoxalic semialdehyde. But since the product is obtained in considerable yield under conditions in which mesoxalic semialdehyde is stable, it appears more probable that the initial product is glycolurilcarboxylic acid, $C_4H_5N_4O_2 \cdot CO_2H$ (isomeric with pseudo-uric acid), which then loses carbon dioxide to give glycoluril.

By modification of the conditions, it is yet hoped that it may be possible to isolate this glycolurilcarboxylic acid, or perhaps, by isomeric change, to obtain pseudo-uric or uric acids. If the carbamide salt of dihydroxymaleic acid is oxidised with mercuric chloride under similar conditions to those above-mentioned, the product is a dark brown, very sparingly soluble substance, which differs from glycoluril in that it dissolves in strong nitric acid to an intense crimson-red solution. This product has yet to be identified.

Relation of Mesoxalic Semialdehyde to Tartronic Acid.—It was pointed out above that a solution of mesoxalic semialdehyde is fairly stable in acid solution, and that when decomposition does take place, by continued heating or evaporation, the products are, mainly at any rate, glyoxal and carbon dioxide. In presence of alkalis, however, the semialdehyde is quickly changed on heating, the product in this case being tartronic acid.

This change was illustrated in the following manner. A solution of the semialdehyde was divided into two parts, and one part was made alkaline with sodium carbonate in the cold, acidified with acetic acid, and precipitated with lead acetate. The resulting white precipitate was then well washed, suspended in water, and decomposed with hydrogen sulphide, avoiding excess; on adding phenylhydrazine acetate to the solution so obtained, the bright orange precipitate of Nastvogel's osazone was obtained, the semialdehyde having undergone little if any change. The other part of the original solution was treated exactly in the same manner, except that after addition of sodium carbonate the alkaline solution was heated on a water-bath at 90—100° for about 15 minutes. In this case, the solution, after acidification with acetic acid, no longer reacted with phenylhydrazine acetate, and the acid solution resulting after decomposition of the lead salt with hydrogen sulphide, when evaporated to small bulk and allowed to stand, set to a mass of transparent crystals. These were recognised by all their properties to be tartronic acid. After drying at 100°, they melted at 158—159° (compare Trans., 1898, **73**, 74), and without recrystallisation furnished the following result on analysis:

0·1995 gave 0·2142 CO_2 and 0·0599 H_2O. C = 29·28; H = 3·33.

$C_3H_4O_5$ requires C = 30·00; H = 3·33 per cent.

The yield of tartronic acid, calculated from the weight of dihydroxy-

maleic acid originally taken, amounted to about 60 per cent. of that required by theory; bearing in mind, however, the unavoidable loss involved in the several operations, there is little doubt that the actual yield is much greater than this. This change, like that of glyoxal to glycollic acid, is an illustration of the great readiness with which the group $-CO\cdot CHO$ is transformed, in presence of alkalis, to $-CH(OH)\cdot CO_2H$.

The facts here recorded have an interesting bearing on the mode of decomposition of dihydroxytartaric acid when its aqueous solution is heated (*loc. cit.*, p. 73). The products are in this case only tartronic acid and carbon dioxide. Addition of hydrochloric acid appears only to have the effect of making the dihydroxytartaric acid more stable; such a mixture may be evaporated on a water-bath almost to dryness without complete destruction of the dihydroxy-acid, but the decomposition products are here again only tartronic acid and carbon dioxide.

No mesoxalic semialdehyde or glyoxal has been detected at any stage of this decomposition, and this fact would appear to exclude the very plausible hypothesis that mesoxalic semialdehyde is the initial product, for under exactly similar conditions mesoxalic semialdehyde would either remain undecomposed or would yield glyoxal. It is evident, therefore, that the generally accepted formula for dihydroxytartaric acid does not convey a clear indication of this decomposition.

With the *salts* of dihydroxytartaric acid, however, the case is different, since, in reference to the experiments here mentioned, the formation of a tartronate would, according to the above hypothesis, be expected, the mesoxalic semialdehyde first formed being changed to tartronic acid in presence of the resulting alkali.

Formation of Glycollic Aldehyde.

Dihydroxymaleic acid, when heated with water to about 50—60°, rapidly loses carbon dioxide and is converted nearly quantitatively to glycollic aldehyde (Trans., 1895, 67, 774). The dry acid undergoes no change when heated to this temperature—or even at 90—100°—nor does it decompose when heated under boiling benzene or chloroform. The addition of a few drops of water, however, to the hot mixture causes an immediate evolution of carbon dioxide. The hypothesis previously suggested to account for these facts (*loc. cit.*, 777) was that combination with water first takes place to produce trihydroxysuccinic acid, and that this then loses two molecules of carbon dioxide, giving glycollic aldehyde hydrate.

It had recently been observed, however, that the perfectly dry acid, $C_4H_4O_6$, decomposes completely and smoothly when heated with dry

pyridine to 50—60°. After distilling off the pyridine under reduced pressure, crystals of glycollic aldehyde appear in the neck of the flask and may be purified from any adhering pyridine by washing with ether.

This fact therefore appears to show that the decomposition is rather to be ascribed to the instability of the negative ion, $C_2(OH)_2(CO_2)_2$, and is therefore conditioned by the ionising capacity of the solvent employed.

When alcohol is used as solvent, decomposition takes place only very slowly on long boiling. The product in this case is different from glycollic aldehyde, and its nature has yet to be determined.

Attempts are being made so to arrange the conditions under which decomposition is effected that only one molecule of carbon dioxide is lost from one molecule of the acid—a change which does occur when simultaneous oxidation takes place—and if this could be accomplished the result should be, as before mentioned, either dihydroxyacrylic acid, tartronic semialdehyde, or hydroxypyruvic acid.

Many other interesting properties of dihydroxymaleic and dihydroxytartaric acids and their derivatives are still under investigation, and it is hoped that the results will shortly be ready for publication.

From the accounts given in this and in former communications, it will be evident that, starting with dihydroxymaleic acid, it is easy to prepare, in either one or two simple operations, any of the following compounds—*dihydroxytartaric acid, tartronic acid, mesoxalic acid, glycollic aldehyde, mesoxalic semialdehyde glyoxal, pyrazinedicarboxylic acid.* In view of these and many other applications, it is hoped that chemical manufacturers may see their way to prepare and supply dihydroxymaleic acid as a commercial article.

In conclusion, the author desires to acknowledge the very valuable assistance which he has received during a considerable portion of these later researches from the co-operation of Mr. J. H. Ryffel, M.A., of Peterhouse, Cambridge, and Guy's Hospital, and to place on record his high appreciation of Mr. Ryffel's scientific enthusiasm and analytical skill.

Most of the materials employed in carrying out these researches have been obtained with the assistance of funds kindly supplied by the Government Grant Committee of the Royal Society.

LXXXIII.—*Behaviour of Solutions of Propyl Alcohol towards Semi-permeable Membranes.*

By ALEXANDER FINDLAY and FREDERICK CHARLES SHORT.

THE problem of the nature of solution is one which has during the past twenty years claimed the attention of many chemists and physicists, and the phenomena of osmosis and the behaviour of semi-permeable membranes have entered largely into its discussion. By reason of the importance of these phenomena and their bearing on the fundamental nature of solution, the crucial experiment carried out by S. U. Pickering, and described by him in the following manner, seemed endowed with special interest. Professor Pickering states (*Ber.*, 1891, 24, 3639): "Eine Lösung von Alkohol in Wasser (57 p. Ct.) wurde in ein poröses Gefäss gebracht und dieses in Wasser gestellt; es zeigte sich, dass das Wasser in die Lösung eintrat. Das poröse Gefäss mit der Lösung wurde darauf in Alkohol getaucht und ich fand, dass der Alkohol in die Lösung eindrang. Das poröse Gefäss war also sowohl für Wasser als auch für Alkohol durchlässig, nicht aber für eine Mischung beider Flüssigkeiten; eine solche Mischung muss daher aus grösseren Molekülen bestehen als jede der reinen Flüssigkeiten, und diesem Umstande muss die Existenz des osmotischen Druckes zugeschrieben werden, nicht aber der Undurchlässigkeit des Diaphragmas für die gelöste Substanz, wie man bisher angenommen hat. Ich habe bis jetzt nur einige wenige vorläufige Versuche angestellt, sie lassen aber keinen Zweifel über die in Rede stehende Thatsache."

In the passage just quoted, it is stated that alcohol (by which one would understand ethyl alcohol) was employed; but Professor Pickering has elsewhere mentioned (for example, *Nature*, 1897, 55, 224) that the alcohol used was propyl alcohol.

Although various allusions to the above experiments are to be found in the literature, no further details are given as to the way in which the experiments were carried out or as to the height to which the liquid rose in the manometer (if one was used), nor is it stated whether the rise was a temporary or a permanent one. The different references made by Pickering to his experiments, also, vary with regard to whether a simple porous pot or a semi-permeable membrane was employed.* Such being the case, the importance attaching to these results made it desirable to repeat the experiments, as far as possible, especially with the view of discovering whether similar

* Professor Pickering has explained to me in a letter that a porous pot only was used, the porosity of which was, however, very small.—A. F.

results could be obtained with other alcohols or other substances. Although, in absence of all experimental details, we cannot be sure that the conditions under which we worked were the same as those under which Pickering's experiments were carried out, we can probably assume that our experiments were at least carried out in a similar manner, and might have been expected to yield similar results. It may, however, be at once stated that, working as we did, we entirely failed to obtain any confirmation of the anomalous behaviour described by Pickering.

For our first experiments, which were repeated at a later date with a different pot, we also made use of a porous pot without semi-permeable membrane. The pots used were ordinary cylindrical, white clay pots, such as are sold for battery purposes, and had a capacity of about 100 c.c. The pots were not specially prepared, except that they were soaked in distilled water, and the air removed from the pores by reduction of pressure. After the pot had been roughly dried by means of filter paper, it was filled with a solution of propyl alcohol (Kahlbaum's "commercial") containing 57 per cent. of alcohol by volume. It was then furnished with a tightly-fitting india-rubber bung and an open manometer tube having a bore of about 2 mm. When the pot with the solution was placed in pure water or in the commercial propyl alcohol, the liquid in the manometer tube, which stood initially from one to two feet above the top of the pot, *fell* in each case; no indication even of a temporary rise was obtained, except, indeed, in one case when air had accidentally got inside the pot.

As the experiments with porous pots alone gave entirely negative results, it was decided to employ a semi-permeable membrane, especially as Pickering has himself stated that a better result might in that case be expected. As semi-permeable membrane we used copper ferrocyanide, which, as Tammann's experiments would show (*Wiedemann's Annalen*, 1888, **34**, 299), is semi-permeable to an aqueous solution of propyl alcohol.

A series of experiments was first of all carried out in duplicate, using two pots of about 170 c.c. capacity, furnished with a copper ferrocyanide membrane, prepared some time previously according to the directions given by Pfeffer. The air was removed from the pores, as described above, and the pots then filled with a solution of propyl alcohol, furnished with a manometer tube and placed in a beaker containing distilled water and standing in a thermostat at 25°. Although solutions of propyl alcohol of different concentration were employed, namely, 10, 30, 70, and 90 per cent. of alcohol by volume, the result was the same in each case; when the semi-permeable membrane was surrounded by water, the liquid in the manometer rose, and continued to do so until it reached the top of the tube—a rise of more

than a metre. The pot was generally allowed to stand in water for at least twenty-four hours, sometimes for several days, during which time the liquid continued to overflow from the open end of the manometer tube. The rise of liquid, therefore, did not seem to be a temporary one. The pot was then removed from the water and placed in propyl alcohol. When this was done the liquid in the manometer began to fall almost immediately, and after several hours fell to the bottom of the manometer, or even retreated within the pot. This fall was in no way due to any leak past the cork or manometer tube, since, when the pot was replaced in water, the liquid again rose in the manometer; and the rise and fall could be obtained repeatedly by placing the pot alternately in water and propyl alcohol.

Although exactly the same results were obtained in the duplicate experiments, a similar series of experiments was also carried out with a third smaller pot which had been furnished with a freshly-prepared copper ferrocyanide membrane. The same results were obtained as in the preceding experiments. Special experiments were also carried out with a 75 per cent. solution of propyl alcohol, but with no different result.

As will be seen, our results are in no way in harmony with those obtained by Pickering; nor can we, in consequence of the uncertainty as to the precise conditions under which those results were obtained, offer any definite explanation of the discrepancy.

Apart, however, from our failure to reproduce Pickering's results, it is somewhat difficult to find a theoretical basis for the possibility of such results. Assuming that the rise of liquid which was obtained by Pickering was only a temporary one, an explanation of the behaviour might be found in differences in the velocity of diffusion of the water and propyl alcohol. The discrepancy between the results obtained by Pickering and by ourselves might, then, be due to differences in the porosity of the pots. This appears to us to be much more plausible than the explanation given by Pickering, which assumes the formation of a molecule so large as to be incapable of passing through the pores of the pot. The comparison of a semi-permeable membrane with a sieve may be a legitimate one so long as the membrane is semi-permeable and its "pores" are of molecular dimensions; but it is difficult to imagine that this can be the case with what one ordinarily terms a porous membrane, the pores of which are not of molecular size.

Another direction in which one might look for an explanation of Pickering's results is in the phenomena of capillarity. If the walls of the porous pot are regarded as consisting of a large number of very minute capillary tubes, a rise of liquid in the pot might be due to surface tension effects. If the surface tension of the liquid inside the pot is greater than that outside, passage of liquid from the outside to

the inside will take place, and a rise will therefore be obtained in the manometer tube. This might account for the rise in the case where the pot was surrounded with propyl alcohol, the surface tension of which is less than that of the solution, but it would not account for the rise in the case when water was outside.

We are forced, therefore, to conclude that the anomalous behaviour of solutions of propyl alcohol in water described by Pickering, unless confirmed by other experiments, is to be accounted for most probably (if the possibility of experimental error is excluded) by differences in the velocity of diffusion. If this be so, the rise of liquid in the pot could only have been temporary, and the experiment would hence lose all its significance for the problem of solution (compare Proc., 1905, **21**, 170).

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LXXXIV.—*Oxymercuric Perchlorates and the Action of Alcohol on Mercury Perchlorates.*

By MASUMI CHIKASHIGÉ.

THE following statements have already been published, in part by Serullas in 1830 and in part by the author in 1895 (Trans., **67**, 1013). Mercuric perchlorate crystallises with six mols. of water, is exceedingly soluble in water, and very deliquescent; it partly decomposes with hot water, and loses both acid and water when left in a desiccator. Alcohol converts it into a white basic compound and gives with its aqueous solution an orange precipitate consisting mainly of mercuric oxide. The white basic compound also leaves a little mercuric oxide when acted on by water. An apparently definite, although amorphous, oxymercuric perchlorate, $O_2Hg_3(ClO_4)_2$, is obtained by heating the normal salt slowly to 150°. Towards both water and alcohol, mercurous perchlorate, which crystallises with four mols. of water, behaves in somewhat the same way as the mercuric salt, except that alcohol has no immediate effect on its aqueous solution. A mixture of mercurous and mercuric perchlorates is obtained when an alcoholic solution of the mercuric salt is boiled and concentrated by evaporation. The author has since made a fuller and a quantitative examination of the subject, the results of which are described in the present paper. Several new salts have been prepared.

Hydrated Oxymercuric Perchlorate, $OHg_3(ClO_4)_4,12H_2O$.—If, instead of just neutralising perchloric acid with mercuric oxide, the solution

of the acid is digested with excess of the oxide and then filtered through asbestos and concentrated by evaporation on the water-bath to a sufficient extent, it will, when left in a desiccator to cool and evaporate, deposit prismatic crystals resembling those of the normal salt except in being somewhat opaque. Dried under cover on a porous tile, the salt has been found to be very soluble in water, leaving only a very little yellow mercuric oxide undissolved, but when its solution is evaporated the salt gradually decomposes into mercuric oxide and the normal perchlorate. The mercury found in it was 48·80 per cent., the calculated amount being 48·76.

Action of Alcohol in the Cold on Mercury Perchlorates.—When either mercuric or mercurous perchlorate is treated with cold alcohol, most of the salt goes into solution. The author now doubts whether the residue is basic to any considerable extent, or much else than anhydrous or at least dehydrated normal salt. In the case of the mercuric salt, the white substance quickly dissolves when the alcohol is being heated to boiling, whilst in the case of the mercurous salt it almost completely dissolves when boiled for a few minutes with the alcohol. That both residues are decomposed when washed with water is no proof of their being basic, because water itself decomposes the hydrated normal salts to some extent. It has not been possible to get enough of the mercuric compound in a sufficiently pure state for analysis, but the mercurous compound has given about 63 per cent. of mercury, the calculation for anhydrous mercurous perchlorate requiring 66·8 and for the hydrated salt 59·6.

Action of Boiling Alcohol on Mercuric Perchlorate.—On boiling the solution of mercuric perchlorate with alcohol, the insoluble matter goes quickly into solution in the manner just indicated, but its dissolution is soon followed by the production of a scanty flocculent precipitate, which, on continuing the boiling, gradually gives place to a very small quantity of granular precipitate rapidly settling at the bottom of the flask. During the boiling, much aldehyde is produced and most of the mercury perchlorate is changed into mercurous perchlorate, and without the formation of any chloride whatever. The change of the mercuric into mercurous salt is never complete. After filtering from the generally insignificant amount of precipitated mercuric salts, the addition of hydrochloric acid gives quantities of mercurous chloride amounting to 91 to 92 per cent. of the total mercury taken as normal mercuric salt, namely, 35·9, 35·1, 36·2 per cent., as against 39·45 per cent. in the normal mercuric salt. The rest of the mercury which remains in the mother liquor and in the small precipitates filtered off is entirely in the mercuric state.

If the alcoholic solution is diluted with water and evaporated, it deposits, on cooling, principally the hydrated mercurous perchlorate.

When, without addition of water, the alcoholic solution is evaporated over briskly boiling water, the mercurous salt is for the most part decomposed into metallic mercury and oxymercuric perchlorates, some perchloric acid no doubt remaining in the solution, for the basic salt is insoluble in acids. When, instead of proceeding in either of these ways, the alcoholic solution is evaporated at a gentle heat, it deposits, towards the end, needle-shaped crystals, coloured slightly grey through contamination with a very little metallic mercury. Some of these crystals were weighed out for analysis, dissolved in water, and filtered from metallic mercury. From the clear solution, mercurous chloride was precipitated and weighed. After removal of all the mercury from another portion of the salt the perchloric acid was precipitated and weighed with the usual precautions as potassium salt.

	Found		$10(HgClO_4)_2,Hg(ClO_4)_2$ requires
ClO_4	34·80	—	34·25
Hg^I	—	62·37	62·62
Hg^{II}	—	—	3·13

The existence of $10(HgClO_4)_2,Hg(ClO_4)_2$ as an individual substance is open to doubt, but it may be pointed out that Rây has found that mercurous nitrite, when treated with water, deposits mercury and tends to form the compound $(HgNO_2)_2,4Hg(NO_2)_2$, not more than 78 per cent. of the mercurous nitrite becoming converted into mercuric nitrite (Trans., 1897, 71, 340).

Action of Boiling Alcohol on Hydrated Oxymercuric Perchlorate.— When hydrated oxymercuric perchlorate is boiled with alcohol, there is formed, at first, an abundant flocculent precipitate, but as the boiling continues, this gradually gives place to a granular precipitate quickly settling down, which is not changed by longer boiling with alcohol. The mother liquor of these precipitates contains much mercurous perchlorate, thus resembling the solution obtained by boiling the normal salt with alcohol. The flocculent and the granular precipitates are distinct oxymercuric perchlorates.

Anhydrous 1/3-Basic Oxymercuric Perchlorate, $OHg_3(ClO_4)_4$.—When the flocculent, white precipitate produced on boiling the hydrated 1/3-basic oxymercuric perchlorate (p. 822) with alcohol appeared to be close to its maximum quantity and had not begun to give place to the dense granular precipitate, it was filtered off, washed well with water, and dried in a steam oven. It is insoluble in either hydrochloric or nitric acid, but is decomposed and dissolved by a mixture of the two. Heated over the Bunsen flame, it remains unchanged until its temperature reaches nearly to that of dull redness, when it seems to burn explosively with a feeble violet flame and leaves a red residue of

mercuric oxide. It behaves, therefore, when heated, much like mercury fulminate, but in a far less violent way. The percentage of mercury was found to be 60·35, whereas theory requires 59·18.

β-2/3-Basic Oxymercuric Perchlorate, $O_2Hg_3(ClO_4)_2$.—The white, granular precipitate, which remains when the alcoholic solution of the hydrated 1/3-basic oxymercuric salt is boiled until there is no sign of further decomposition being in progress, was collected and prepared for examination in the same way as the foregoing salt; it is called the β-salt in order to distinguish it from the 2/3-basic oxymercuric perchlorate, described by the author in his first paper as being produced by heating the normal salt. Its analysis gave 70·73 and again 71·15 per cent. of mercury, whereas the calculated amount is 72·21.

In solubility in water and single acids it resembles the 1/3-basic salt, and in this respect differs from the α-2/3-basic salt, which is decomposed by water and dissolved by acids. Up to nearly a red heat, the β-2/3-basic salt, like the α-2/3-basic salt and the 1/3-basic salt, is quite stable. But at about a dull red heat it detonates with great violence and entirely disappears. The violence of its detonation is certainly much greater than that of the detonation of an equal weight of mercury fulminate. A milligram of the salt shattered the end of a nickel spatula on which it was exploded. The α-salt, on the other hand, decomposes without the least explosion at a temperature nearly sufficient to decompose mercuric oxide. The β-salt also detonates by percussion. Ordinary percussion caps have been found to detonate satisfactorily when charged in the usual way with a mixture of 37·5 parts each of the β-salt and potassium chlorate to 25 parts of antimony sulphide.

Nature of the Action of Alcohol on Mercury Perchlorates.—From what has been stated, it seems fairly certain that alcohol in the first place removes the water from the three hydrated salts: the mercuric and the 1/3-basic oxymercuric perchlorates and the mercurous perchlorate; then it acts, at a boiling heat, on mercuric perchlorate as a reducing agent, converting it into mercurous perchlorate and perchloric acid:

$$2Hg(ClO_4)_2 + C_2H_6O = (HgClO_4)_2 + 2HClO_4 + C_2H_4O.$$

The aldehyde and the perchloric acid volatilise, the latter possibly in part as its ester, but probably not, in accordance with Roscoe's experiments as to the behaviour of the acid with alcohol (*Proc. Roy. Soc.*, 1862, **11**, 502; *J. Chem. Soc.*, 1862, **15**, 213).

The alcohol evidently acts in such a way on the 1/3-basic oxymercuric salt as to resolve it into normal mercuric and β-2/3-basic oxymercuric perchlorates; then by reduction the alcohol converts most of the former into perchloric acid and mercurous perchlorate, in the manner just shown. The very slight production of oxymercuric

perchlorate when the alcoholic solution of either mercuric or mercurous perchlorate is boiled is certainly to be attributed to hydrolysis; at the same time, the mercurous salt becomes, although to a small extent only, resolved into metal and mercuric salt.

In conclusion, the author wishes to express his warmest thanks to Dr. Edward Divers for undertaking the thorough revision of the paper.

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LXXXV.—*Studies in the Camphane Series. Part XX. Camphorylazoimide.*

By Martin Onslow Forster and Hans Eduard Fierz.

By their investigation of semicarbazide, Thiele and Stange showed (*Ber.*, 1894, **27**, 31, and *Annalen*, 1894, **283**, 1) that a solution of the hydrochloride, when treated with sodium nitrite, yields carbaminoazoimide,

$$NH_2\cdot CO\cdot NH\cdot NH_2 + HNO_2 = NH_2\cdot CO\cdot N{<}\begin{matrix}N\\ \| \\ N\end{matrix} + 2H_2O.$$

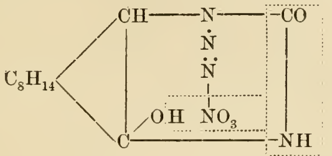
In view of the tertiary character of the nitrogen atom to which the amino-group in camphoryl-ψ-semicarbazide is attached (compare this vol., p. 722), the possibility of obtaining camphorylazoimide by the action of nitrous acid appeared somewhat remote. Nevertheless, we find that sodium nitrite, when added to an aqueous solution of camphoryl-ψ-semicarbazide nitrate, causes the immediate precipitation of camphorylazoimide, owing to simultaneous elimination of cyanic acid:

$$C_8H_{14}{<}\begin{matrix}CH\cdot N(NH_2)\\ | \\ C(OH)-NH\end{matrix}{>}CO + HNO_2 = C_8H_{14}{<}\begin{matrix}CH\cdot N_3\\ | \\ CO\end{matrix} + HNCO + 2H_2O.$$

In seeking for the explanation of this change, it is necessary to recall the behaviour of diazoguanidine nitrate, which has been shown by Thiele (*Annalen*, 1892, **270**, 1) to yield cyanamide and azoimide under the influence of alkalis:

$$\begin{array}{lll} H\cdot N & \text{———————} & -C{:}NH \\ \dot{N} & & \quad | \\ \ddot{N}- & -NO_3 \quad H- & -NH \end{array} \quad .$$

It is not unlikely that the action of nitrous acid on camphoryl-ψ-semicarbazide nitrate involves the momentary production of a diazo-derivative, from which camphorylazoimide would arise by eliminating nitric and cyanic acids:



Attempts to isolate this compound, which would correspond to the extraordinarily stable diazoguanidine nitrate, have not been successful.

The alternative explanation which suggests itself is not supported by facts. It might be supposed that when concentrated nitric acid acts on acetone camphoryl-ψ-semicarbazone, the salt produced is the nitrate of normal camphorylsemicarbazide,

$$C_8H_{14}<\begin{matrix}CH\cdot N(NH_2)\cdot CO\cdot NH_2,HNO_3,\\ |\\ CO\end{matrix}$$

corresponding to Rupe's camphorylcarbamide, because we have already shown that whilst alkalis transform the last-named substance into camphoryl-ψ-carbamide, the converse change is brought about by acids. If the same relationship connected the semicarbazides, the nitrate obtained from acetone camphoryl-ψ-semicarbazone should yield with aldehydes a series of semicarbazones distinct from those described in our previous communication (this vol., p. 727), all of which were prepared from the acetic acid solution of freshly reduced camphorylnitroso-ψ-carbamide. This, however, is not the case. A specimen of benzylidene camphoryl-ψ-semicarbazone has been prepared from benzaldehyde and camphoryl-ψ-semicarbazide nitrate, and found to be identical with the substance already described (*loc. cit.*).

Although readily fusible, camphorylazoimide crystallises with unusual ease; its behaviour when superheated resembles that of phenylazoimide and its *p*-nitro-derivative, energetic decomposition taking place without actual detonation. An unusual feature is its failure to yield hydrazoic acid with alkalis or acids, but it must be remembered that whilst the acylazoimides readily yield hydrazoic acid on hydrolysis, phenylazoimide resists the action of acids and alkalis, yielding diazoimide only when converted into the *p*-nitro-derivative; with this in mind, we have tried to prepare substituted camphorylazoimides, hitherto without success. Moreover, the substance under discussion represents a type of azoimide distinct from that of hippurylazoimide, phenylazoimide, benzylazoimide, and the recently described

methylazoimide (Dimroth and Wislicenus, *Ber.*, 1905, **38**, 1573), attachment of the azoic nucleus in camphorylazoimide occurring at a carbon atom which forms the unit of a fully hydrogenated cycloid instead of an open chain or a benzene ring.

In other respects, however, the behaviour of camphorylazoimide agrees with that of other nitrides. Reduction with zinc and acetic acid gives rise to aminocamphor, and a solution of stannous chloride in hydrochloric acid liberates two-thirds of the azoic nitrogen, as in the case of carbaminoazoimide (Thiele and Stange, *Annalen*, 1894, **283**, 1):

$$C_8H_{14}<\overset{CH\cdot N_3}{\underset{CO}{|}} + H_2 = C_8H_{14}<\overset{CH\cdot NH_2}{\underset{CO}{|}} + N_2.$$

The same proportion of nitrogen is eliminated when alcoholic alkalis act on the substance, the product consisting of a new compound, α-iminocamphor:

$$C_8H_{14}<\overset{CH\cdot N_3}{\underset{CO}{|}} \longrightarrow C_8H_{14}<\overset{CH:N}{\underset{CO}{|}} \longrightarrow C_8H_{14}<\overset{C:NH}{\underset{CO}{|}}.$$

This curious change, which takes place quantitatively, recalls the behaviour of benzylazoimide towards acids, Curtius and Darapsky having shown (*J. pr. Chem.*, 1901, ii, **63**, 428) that among other products benzaldehyde and ammonia are formed, doubtless arising from the intermediate imino-compound, $C_6H_5\cdot CH:NH$.

It will be observed that α-iminocamphor is the monoimine of camphorquinone, and, as would be foreseen from the recent work of Willstätter, Eugen Meyer, and Pfannenstiel (*Ber.*, 1904, **37**, 1494 and 4605), the solid substance is highly unstable. A few minutes after being spread on porous earthenware it undergoes spontaneous change, which takes place suddenly if the material is pressed together in a compact mass; at the same time, white fumes are evolved, and considerable rise of temperature occurs. α-Iminocamphor is indifferent towards alkalis, but is readily soluble in dilute acids, which resolve it quantitatively into camphorquinone and ammonia:

$$C_8H_{14}<\overset{C:NH}{\underset{CO}{|}} + H_2O = C_8H_{14}<\overset{CO}{\underset{CO}{|}} + NH_3.$$

It was expected that hydrogen peroxide would transform iminocamphor into *iso*nitrosocamphor, Haase and Wolffenstein having shown (*Ber.*, 1904, **37**, 3228) that the product from piperidine and hydrogen peroxide, previously regarded as δ-aminovaleraldehyde, consists of piperidine oxide, $C_5H_{10}N\cdot OH$ or $C_5H_{10}NH:O$, but although the empirical result in both cases is the same, namely, addition of an oxygen atom, α-camphornitrilic acid is produced instead of *iso*nitroso-

camphor. We suspect this change to depend on the intermediate formation of the *pseudo*-modification of *iso*nitrosocamphor,

$$C_8H_{14}<\begin{matrix}C:NH\\ |\\ CO\end{matrix} \rightarrow C_8H_{14}<\begin{matrix}C=N-OH\\ |\\ C(OH)\cdot OH\end{matrix} \rightarrow$$

$$C_8H_{14}<\begin{matrix}C\equiv N\\ |\quad\ |\\ C(OH)\cdot O\end{matrix} \rightarrow C_8H_{14}<\begin{matrix}CN\\ CO_2H\end{matrix}.$$

Attempts to isolate this compound in the form of its colourless benzoyl derivative have been unsuccessful.

Although α-iminocamphor is so extremely prone to change, it may be arrested in the form of a stable carbamide by adding the calculated amount of bornylcarbimide to a solution of the freshly-prepared substance in light petroleum. The derivative thus obtained can be recrystallised and heated considerably above 100° without undergoing alteration, but hot dilute acids resolve it into camphorquinone and bornylcarbamide. It is interesting to compare the specific rotatory power of the new compound with that of camphorylbornylcarbamide (this vol., p. 120), from which it differs only by the possession of one double linkage :

$$C_8H_{14}<\begin{matrix}CH\cdot NH\cdot CO\cdot NH\cdot C_{10}H_{17}\\ |\\ CO\end{matrix}$$

s-Camphorylbornylcarbamide.
$[\alpha]_D$ 28·6°.

$$C_8H_{14}<\begin{matrix}C:N\cdot CO\cdot NH\cdot C_{10}H_{17}\\ |\\ CO\end{matrix}$$

Bornylcarbiminocamphor.
$[\alpha]_D$ 153·8°.

It remains to be mentioned that although camphorylazoimide is precipitated on adding sodium nitrite to an aqueous solution of camphoryl-ψ-semicarbazide nitrate, the action takes a different course when the acetate is the salt employed; in presence of a slight excess of acetic acid, nitrous oxide is liberated and crystals of camphoryl-ψ-carbamide separate :

$$C_8H_{14}<\begin{matrix}CH\cdot N(NH_2)\\ |\\ C(OH)-NH\end{matrix}>CO + HNO_2 = N_2O + H_2O +$$

$$C_8H_{14}<\begin{matrix}CH-NH\\ |\\ C(OH)\cdot NH\end{matrix}>CO.$$

Thiele also (*loc. cit.*) observed that aminoguanidine nitrate behaved differently from the acetate towards sodium nitrite, but the liberation of nitrous acid was not recorded.

EXPERIMENTAL.

Camphorylazoimide, $C_8H_{14}<\begin{matrix}CH\cdot N_3\\ |\\ CO\end{matrix}$.

Thirty-five grams of camphoryl-ψ-semicarbazide nitrate were dissolved in 200 c.c. of water, and, the solution having been cooled with ice, 8 grams of sodium nitrite crystals were added in small quantities. Turbidity was developed immediately, but no evolution of gas occurred at the outset. When, roughly, one-half the nitrite had been added, a white, crystalline precipitate was formed, and the transparent, gummy mass which had previously accumulated began to harden; simultaneously, the pungent odour of cyanic acid became perceptible, and towards the end of the reaction disengagement of this gas became quite brisk. After an hour, the substance was filtered and dried, the yield being 90 per cent. of the theoretical amount; the neutralised filtrate, when concentrated on the water-bath, developed the vivid blue coloration with cobalt nitrate in acetic acid which is characteristic of cyanates.

Camphorylazoimide crystallises from alcohol in transparent, hexagonal prisms, which usually become aggregated in lustrous plates; it melts at 67°, and when heated in a dry tube decomposes suddenly without exploding. If protected from light, the freshly crystallised substance retains its lustre indefinitely, but a few minutes' exposure to sunlight renders the crystals dull and opaque.

0·1830 gave 0·4163 CO_2 and 0·1334 H_2O. C = 62·04; H = 8·10.
0·1574 „ 29·9 c.c. of nitrogen at 20° and 762 mm. N = 21·79.
$C_{10}H_{15}ON_3$ requires C = 62·17; H = 7·77; N = 21·76 per cent.

The substance is readily volatile in steam, the vapour having a pleasant camphor-like odour; it does not reduce Fehling's solution or ammoniacal silver oxide, and bromine appears to have no substituting action. It is moderately soluble in boiling water and in cold absolute alcohol, dissolving freely in ethyl acetate, acetone, and light petroleum. Determinations of rotatory power were carried out in a 2-dcm. tube, 25 c.c. of solvent being employed in each case.

0·2608 gram in benzene gave α_D − 7°20′, whence $[\alpha]_D$ − 351·5°.
0·2602 „ in absolute alcohol gave α_D − 5°55′, whence $[\alpha]_D$ − 284·2°.
0·2610 „ in acetone gave α_D − 5°50′, whence $[\alpha]_D$ − 279·4°.
0·2589 „ in chloroform gave α_D − 5°6′, whence $[\alpha]_D$ − 246·2°.

All attempts to obtain azoimide from the camphoryl derivative have been fruitless. The substance was treated with boiling 20 per cent.

sulphuric acid under a reflux condenser, to the upper end of which were attached bulbs containing aqueous sodium hydroxide; there was no trace of sodium nitride after one hour, and 50 per cent. sulphuric acid merely charred the material without eliminating hydrazoic acid. In neither case was there any sign of camphorquinone, but this substance is quickly formed when camphorylazoimide is heated with dilute aqueous sodium hydroxide; hydrazoic acid cannot be detected in the alkaline liquid, however. Equally unsuccessful were experiments in which the compound was heated in sealed tubes with aqueous and alcoholic solutions of silver nitrate; in both cases, silver was deposited, unaccompanied by silver nitride.

Reduction with Zinc and Acetic Acid.—Three grams of the azoimide were dissolved in 30 c.c. of glacial acetic acid and treated with 5 grams of zinc dust; after 12 hours, the liquid was heated on the water-bath, filtered, and treated with excess of potassium hydroxide, which precipitated aminocamphor. The base was identified by conversion into camphorylcarbamide, which was then transformed into the characteristic carbimide.

Action of Stannous Chloride.—Camphorylazoimide is not much more soluble in hydrochloric acid than in water, but on adding stannous chloride, minute bubbles of gas appear, effervescence continuing during a considerable period if the liquid remains at the ordinary temperature; ultimately the substance dissolves completely, forming a colourless solution. Using weighed quantities, it is found that two thirds of the total nitrogen is liberated in the change.

0·2477 gave 31·9 c.c. of nitrogen at 25° and 773 mm. N = 14·64.
$C_{10}H_{15}ON_3$ requires 2/3N = 14·51 per cent.

In order to identify the other product, 3 grams of the azoimide suspended in 20 c.c. of concentrated hydrochloric acid were treated with 5 grams of stannous chloride. The oily base liberated by excess of potassium hydroxide was extracted with ether, dried with solid potash, and precipitated in the form of carbonate, which was then transformed into Rupe's camphorylcarbamide, and finally into the carbimide.

Action of Concentrated Sulphuric Acid.—When the azoimide is dropped into concentrated sulphuric acid, a very violent change takes place, nitrogen being set free suddenly, with considerable rise of temperature, whilst the acid solution remains clear, but does not become yellow. On repeating the experiment with weighed quantities in a closed vessel communicating with a nitrometer, the proportion of nitrogen evolved was found to be the same as when stannous chloride acts on the substance.

0·2328 gave 28·6 c.c. of nitrogen at 22° and 770 mm. N = 14·10.
$C_{10}H_{15}ON_3$ requires 2/3N = 14·51 per cent.

We have not identified the other products.

a-Iminocamphor (*Camphorquinonemonoimine*), $C_8H_{14}<\begin{matrix}C{:}NH \\ | \\ CO\end{matrix}$.

When aqueous potassium hydroxide is added to an alcoholic solution of camphorylazoimide, a vigorous action takes place accompanied by brisk effervescence; if the colourless liquid is evaporated, it becomes pale yellow, and dilution precipitates an oil which quickly solidifies. This product is soluble in hot water, and dissolves freely in cold alcohol; it does not reduce Fehling's solution or ammoniacal silver oxide, but the aqueous solution becomes yellow immediately on adding a few drops of dilute sulphuric acid, the development of colour being rapidly followed by the formation of a bulky precipitate of camphorquinone, the filtrate from which contains ammonium sulphate. Complete removal of nitrogen from camphorylazoimide can be effected, therefore, in two stages, each of which is reached quantitatively. A tube containing a weighed amount was enclosed in a wide-mouthed bottle placed in communication with a nitrometer filled with water; on tilting the bottle, which contained alcoholic potassium hydroxide, the volume of gas produced could be measured.

0·3045 gave 39·6 c.c. of nitrogen at 23° and 762 mm. N = 14·62.
0·3357 ,, 43·3 c.c. ,, ,, 23° ,, 762 mm. N = 14·50.
$C_{10}H_{15}ON_3$ requires 2/3N = 14·51 per cent.

In order to estimate the nitrogen removed during the second stage of the decomposition, a weighed quantity of camphorylazoimide was dissolved in ether and allowed to float on a few c.c. of a 50 per cent. aqueous solution of pure sodium hydroxide in a small separating funnel; on adding a few drops of absolute alcohol, a vigorous action ensued, and when this had subsided the alkali was removed. The ethereal solution of iminocamphor was agitated with dilute hydrochloric acid, becoming bright yellow in consequence. On evaporating the acid solution, a residue of ammonium chloride was obtained, and from this the platinichloride was prepared as usual.

0·5213 gram azoimide gave 0·2380 Pt. N = 6·58.
0·3472 ,, ,, ,, 0·1689 Pt. N = 7·01.
$C_{10}H_{15}ON_3$ requires 1/3N = 7·25 per cent.

The ethereal solution deposited camphorquinone on evaporation.

Although these experiments leave but little doubt regarding the identity of the product from camphorylazoimide and alcoholic alkali,

α-iminocamphor is so unstable, and so sensitive to the action of acids and of air, that it is not possible to obtain it in purified form. The compound can be isolated by dissolving 2 or 3 grams of camphorylazoimide in pure ether, adding 50 per cent. aqueous potassium hydroxide, and then sufficient absolute alcohol to begin the action; when gas is no longer evolved, the colourless ethereal solution is decanted through a dry filter and quickly evaporated. On adding water to the oily residue, α-iminocamphor is obtained as a crystalline paste, which quickly dries on porous earthenware; it is then only very pale yellow, and easily crumbled, but soon becomes bright yellow and cohesive. No definite melting point can be recorded; a freshly prepared specimen, almost free from colour, melted at 50—60°, and it has been generally noticed that the bright yellow substance into which it changes melts at 120—130°. One specimen was analysed immediately after isolation, and subsequently at intervals of one day and two days, with the following results:

0·1804 gave 0·4554 CO_2 and 0·1528 H_2O. C = 68·84; H = 9·41.
0·1553 „ 0·3883 CO_2 „ 0·1295 H_2O. C = 68·19; H = 9·26.
0·1782 „ 0·4300 CO_2 „ 0·1443 H_2O. C = 66·94; H = 9·26.
$C_{10}H_{15}ON$ requires C = 72·72; H = 9·02 per cent.
$C_{10}H_{15}O_2N$ „ C = 66·30; H = 8·28 „ „

The spontaneous change, therefore, appears to involve addition of oxygen, and although the bright yellow colour of the product suggests the formation of camphorquinone, an intensely yellow specimen which had remained during 8 days in a desiccator containing calcium chloride and potassium hydroxide gave an amount of nitrogen corresponding to 7·74 per cent. ($C_{10}H_{15}O_2N$ requires N = 7·73 per cent.).

On adding ethereal ferric chloride to a freshly prepared solution of iminocamphor, a brown coloration is developed, followed almost immediately by a brown precipitate of ferric hydroxide mixed with camphorquinone.

The specific rotatory power of α-iminocamphor was determined by dissolving a weighed quantity of camphorylazoimide in light petroleum, allowing the solution to float on 50 per cent. potassium hydroxide, and adding 2 drops of absolute alcohol, evolution of nitrogen continuing during one hour; when this had ceased, the alkali was removed, and the filtered petroleum, which was practically colourless, diluted to a measured volume. Thus iminocamphor from 0·7984 gram of camphorylazoimide, dissolved in 50 c.c. of light petroleum, gave α_D 2°30′ in a 2-dcm. tube, whence $[\alpha]_D$ 91·5°. One attempt to determine the specific rotatory power of the freshly isolated α-iminocamphor failed because the substance became hot and emitted white fumes while on the balance-pan; on another occasion, 0·4154 gram dissolved in

25 c.c. of absolute alcohol gave α_D 2°35′ in a 2-dcm. tube, whence $[\alpha]_D$ 77·8°.

Action of Hydrogen Peroxide.—A neutral solution of hydrogen peroxide was agitated with an ethereal solution of α-iminocamphor; rise of temperature took place, but no development of colour occurred. On removing the ethereal portion and evaporating the solvent, α-camphornitrilic acid was obtained; it melted at 148°, and did not depress the melting point of a specimen prepared from *iso*nitrosocamphor.

0·1737 gave 0·4221 CO_2 and 0·1355 H_2O. C = 66·26; H = 8·66.
$C_{10}H_{15}O_2N$ requires C = 66·29; H = 8·28 per cent.

It was hoped that the intermediate stage in this curious change might be recognised by drawing air through a suspension of iminocamphor in water during several days. On filtering the bright yellow product at the end of one week, the liquid was found to be indifferent towards Fehling's solution and ammoniacal silver oxide, giving ammonia with alkali; the yellow solid still contained 4 per cent. of nitrogen, but it has not been possible to obtain from it the "colourless benzoyl derivative of *iso*nitrosocamphor."

Bornylcarbiminocamphor, $C_8H_{14}<\begin{matrix}C:N\cdot CO\cdot NH\cdot C_{10}H_{17}\\ | \\ CO\end{matrix}$.

Two grams of camphorylazoimide were dissolved in 30 c.c. of light petroleum and the solution allowed to float on concentrated aqueous potassium hydroxide; conversion into α-iminocamphor having been effected in the manner described, the filtered petroleum solution was treated with 1·8 grams of bornylcarbimide and transferred to a desiccator. No alteration in the temperature or appearance of the solution was noticeable, but within one hour, minute white needles appeared, accumulating during 12 hours until 3·2 grams were obtained. After being washed with petroleum, the substance melted at 205° becoming bright yellow at about 190°.

0·1319 gave 0·3534 CO_2 and 0·1144 H_2O. C = 73·07; H = 9·63.
0·1868 ,, 13·8 c.c. of nitrogen at 24° and 765 mm. N = 8·34.
$C_{21}H_{32}O_2N_2$ requires C = 73·25; H = 9·30; N = 8·14 per cent.

The following determinations of rotatory power were carried out in a 2-dcm. tube, 25 c.c. of the solvent being employed in each case.

0·3332 gram	in chloroform	gave	α_D 4°6′,	whence	$[\alpha]_D$ 153·8°.
0·2988 ,,	benzene	,,	α_D 3°9′,	,,	$[\alpha]_D$ 131·8°.
0·3513 ,,	acetone	,,	α_D 3°24′,	,,	$[\alpha]_D$ 121·0°.
0·2318 ,,	alcohol	,,	α_D 2°1′,	,,	$[\alpha]_D$ 108·7°.

The substance dissolves readily in the foregoing liquids, more sparingly in boiling light petroleum, from which it crystallises in silky needles, whilst hot concentrated alcoholic solutions deposit lustrous prisms which have a faint yellow colour ; it transmits yellow light, and the solutions in organic media are bright yellow. On adding a few drops of dilute sulphuric acid to an alcoholic solution, the yellow colour disappears, being restored in a more intense shade on boiling the liquid, from which camphorquinone separates on cooling.

Action of Nitrous Acid on Camphoryl-ψ-semicarbazide in Acetic Acid.

The slightly acid solution of camphoryl-ψ-semicarbazide obtained by reducing the nitroso-ψ-carbamide with zinc and acetic acid effervesced slowly when treated with sodium nitrite, and a white, crystalline precipitate separated ; this was filtered and recrystallised from boiling water, which deposited lustrous, white needles, melting and evolving gas at 194°, and yielding the nitroso-compound already described (this vol., p. 116). The temperature is 6° higher than that recorded as the melting point of the ψ-carbamide, doubtless owing to a trace of the normal modification in specimens previously obtained. In fact, the difficulty of completely transforming the *pseudo*-carbamide into the isomeride is greater than we thought at first ; so much so, that the apparent production of camphorylcarbimide by the action of hot water on camphorylnitroso-ψ-carbamide must now be recognised as due to traces of the normal carbamide in the material submitted to the action of nitrous acid.

It has not been difficult to identify the gaseous product as nitrous oxide, and in order to ascertain whether the action proceeds quantitatively on the lines indicated by the equation already given, the gas obtainable from 10 c.c. of solution was measured, and the *pseudo*-semicarbazide present in the same volume of liquid was determined by weighing in a Gooch crucible the semicarbazone precipitated by benzaldehyde.

10 c.c. gave 0·3970 gram of semicarbazone. Available N = 1·78 grams per litre.

10 c.c. gave 32·4 c.c. of nitrous oxide at 24° and 762 mm.
Available N = 1·82 grams per litre.

These results are in sufficiently close agreement to show that all the available nitrogen is removed in the form of nitrous oxide.

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LXXXVI.—*The Action of Magnesium Methyl Iodide on Pinene Nitrosochloride.*

By William Augustus Tilden and Joseph Arthur Stokes, B.Sc.

With the object of further studying pinene nitrosochloride and the circumstances in which the nitroso-derivatives of pinene retain the bimolecular constitution, it was thought that some interest would attach to the replacement of the chlorine of the nitrosochloride by an alkyl group. For this purpose, the use of Grignard's reagent at once suggested itself, and the anticipated reaction has been accomplished. The resulting oxime possesses well developed basic properties, as it readily forms a stable hydrochloride. The proportions of materials employed and the conditions of experiment have been varied in successive operations, but the yield of the oxime remains very small, amounting to less than 10 per cent. of the nitrosochloride used. The by-products are chiefly uncrystallisable and become brown on exposure to the air. They include, however, a notable quantity of an interesting saturated base produced by the interaction of the magnesium alkyl iodide with the oxygen of the nitroso-group, the chlorine of the nitrosochloride remaining undisturbed. The products are represented by the following formulæ:

Pinene nitrosochloride.

$$(C_7H_{12})'' < \begin{matrix} CH_3 \\ | \\ CCl \\ | \\ CH\cdot NO \end{matrix}$$

Bimolecular.

Methylpinone-oxime.

$$(C_7H_{12})'' < \begin{matrix} CH_3 \\ | \\ C\cdot CH_3 \\ | \\ C:NOH \end{matrix}$$

Unimolecular.

The saturated base, chlorhydrodimethylpinylamine.

$$(C_7H_{12})'' < \begin{matrix} CH_3 \\ | \\ CCl \\ | \\ CH\cdot N(CH_3)_2 \end{matrix}$$

Unimolecular.

The unimolecular constitution of this base appears to dispose of any idea that the two molecules of which the nitrosochloride consists are united by the chlorine as well as by the nitroso-group present in each. If the chlorine atoms formed a part of the link it might be expected that the base, which retains the chlorine atom, would be similarly bimolecular.

The chlorinated base readily parts with the elements of hydrogen

chloride, yielding an unsaturated base which is identical with dimethylpinylamine,

$$(C_7H_{12})'' \lessdot \begin{matrix} C\cdot CH_3 \\ \| \\ C\cdot N(CH_3)_2 \end{matrix}.$$

It is remarkable that the chlorine of the chlorinated base is not exchangeable for methyl by the further action of the magnesium methyl iodide used in excess, even at a temperature exceeding 100°. This is a further example of the mutual influence of the groups occupying the ortho-position in these compounds, which is indicated also by the effect produced by the chlorine atom in preventing the conversion of the neighbouring nitroso-group into the oxime form (compare Trans., 1904, **85**, 764).

Experimental.

A solution of magnesium methyl iodide in ether was first prepared by mixing together 3·5 grams of magnesium powder, 25 grams of methyl iodide, and 75 c.c. of dry ether. The clear solution was then added in small quantities to 15 grams of pinene nitrosochloride made into a thin paste with dry ether. After standing at the ordinary temperature some twelve hours, the mixture was heated to the boiling point of the ether for about an hour. A small quantity of alcohol was then added, and the precipitated magnesium hydroxide dissolved by adding a strong aqueous solution of ammonium chloride. After evaporating off the ether, the residual viscid substance was washed with cold water and was then redissolved in ether and shaken in a separating funnel with a small quantity of very dilute hydrochloric acid. The ethereal and acid solutions were then separated. The former on addition of light petroleum gave a white, crystalline precipitate which proved to be the oxime.

The acid solution, rendered slightly alkaline by caustic potash and extracted with ether, yielded large, thick, rhombic prisms melting at 122° and consisting of the chlorinated base.

The by-products from both ethereal solutions were viscid and yellow substances, darkening on exposure to the air, from which nothing definite could be obtained.

The Oxime, $C_{10}H_{15}(CH_3)$:NOH.

The oxime was readily soluble in cold alcohol, ether, benzene, acetone, ethyl acetate, and chloroform, but almost insoluble in petroleum even when hot. After recrystallisation from a mixture of chloroform and petroleum, it was obtained in prismatic needles melting at 193°.

0·2026 gave 13·9 c.c. moist nitrogen at 21° and 768 mm. N = 7·94.
$C_{11}H_{19}ON$ requires N = 7·73 per cent.
0·0310 in 13·2 benzene gave Δt – 0·06°. M. W. = 191.
0·0858 „ „ „ Δt – 0·17°. M. W. = 187.
The unimolecular formula $C_{11}H_{19}ON$ requires 181.

This compound is soluble in warm dilute caustic potash, also in warm dilute hydrochloric acid, yielding a definite hydrochloride which, after recrystallisation from alcohol, gave the following results :

0·2112 gave 0·1402 AgCl. Cl = 16·42.
$C_{11}H_{19}ON,HCl$ requires Cl = 16·32 per cent.

The *benzoyl* derivative, prepared by the conjoint action of benzoyl chloride and caustic potash solution, crystallises from petroleum in plates which melt at 118°.

The *methyl ether*, $C_{10}H_{15}(CH_3)\!:\!NO\cdot CH_3$, was obtained by boiling the oxime dissolved in methyl alcohol with methyl iodide and caustic potash. On pouring the solution into water, the ether was precipitated and was crystallised from methyl alcohol ; it forms small, prismatic needles which melt at 62°.

0·2112 gave 13·7 c.c. moist nitrogen at 21° and 769·5 mm. N = 7·48.
$C_{12}H_{21}ON$ requires N = 7·18 per cent.

Action of Acids on the Oxime.

Two grams, heated in a sealed tube with excess of 20 per cent. hydrochloric acid for about two hours, gave a solution which reduced Fehling's solution, and when submitted to steam distillation gave a sweet-scented oil. The quantity was insufficient for detailed study, but obviously consisted of the corresponding ketone. This was confirmed by mixing it with hydroxylamine and caustic soda, with the addition of a little alcohol, when, after some time, needles of the original oxime were deposited.

The oxime dissolves in warm concentrated sulphuric acid with production of a red colour, which, on admixture of water, disappears, and a precipitate is formed of the original oxime.

Examination of the Chlorinated Base.

The chloro-base was analysed after crystallisation from ether.

0·1564 gave 0·3820 CO_2 and 0·1460 H_2O. C = 66·44 ; H = 10·36.
0·0951 gave 0·0634 AgCl. Cl = 16·51.
0·2340 gave 14·0 c.c. moist nitrogen at 22° and 754·5 mm. N = 6·73.
$C_{12}H_{22}NCl$ requires C = 66·82; H = 10·20; Cl = 16·47; N = 6·50 per cent.

0·0708 in 12·9 benzene gave $\Delta t - 0·12°$. M. W. = 224·1.
0·1362 „ „ „ $\Delta t - 0·23°$. M. W. = 224·9.
The unimolecular formula $C_{12}H_{22}NCl$ requires M. W. = 215·5.

With the object of obtaining the base $C_7H_{12}<\begin{matrix}C(CH_3)_2\\ |\\ CHN(CH_3)_2\end{matrix}$, which would result from the exchange of the chlorine for a methyl group, the pure chloro-base, dissolved in ether, was mixed with an excess of magnesium methyl iodide. It was found, however, that no interaction occurred either at the ordinary temperature or at the boiling point, or when the temperature of ebullition was raised to 60° by addition of toluene. A fresh ethereal solution of the base and reagent, sealed up and heated to about 110°, deposited a liquid and a small quantity of viscid matter, but nothing could be obtained from the product except a minute quantity of volatile alkaline matter, which was too small in amount to permit of its separation from the brown, viscous substances chiefly produced.

The *hydrochloride*, which was prepared by dissolving the base in ether and passing hydrogen chloride into the solution, forms small needles.

0·2887 required 11·6 c.c. of standard silver nitrate, of which 1 c.c. = 0·003548 Cl. Cl = 14·29 per cent.
$C_{12}H_{22}NCl,HCl$ requires Cl (of HCl) = 14·14 per cent.

Action of Alcoholic Potash on the Base.

Five grams of the chlorinated base dissolved in alcohol were boiled with 1·5 grams of caustic potash until the reaction was completed as indicated by the precipitation of potassium chloride. On adding to the liquid a small quantity of water, colourless crystals separated out, which, after recrystallisation from diluted alcohol, melted at 112°.

0·2038 gave 14·2 c.c. of moist nitrogen at 25° and 761 mm. N = 7·83.
$C_{12}H_{21}N$ requires N = 7·82 per cent.

The *hydrochloride* of this *unsaturated base* was obtained in the form of small, white needles by dissolving the base in ether and passing dry hydrogen chloride into the solution.

0·2009 required 9·4 c.c. $N/10$ $AgNO_3$. Cl = 16·59.
0·2742 „ 12·8 c.c. $N/10$ $AgNO_3$. Cl = 16·56.
$C_{12}H_{21}N,HCl$ requires Cl = 16·47 per cent.

As this base was presumably identical with dimethylpinylamine, it was thought probable that it would yield a nitrate more or less resembling the nitrate of pinylamine, which is distinguished by its

slight solubility in water; this was found to be the case. The unsaturated base, dissolved in the smallest possible quantity of hydrochloric acid, gives, on the addition of a solution of sodium nitrate, a precipitate of small prisms which resemble the pinylamine nitrate in solubility.

In order to compare the new base with dimethylpinylamine, which has not hitherto been described, six grams of pinylamine were dissolved in methyl alcohol and heated with an excess of methyl iodide at 100° for some hours. After evaporating off the excess of methyl iodide, the liquid was poured into dry ether. A white, crystalline precipitate of the hydriodide was deposited, whilst the mother liquor retained a yellow, viscid oil.

The hydriodide is very soluble in water and gave an immediate precipitate with silver nitrate.

0·2168 gave 0·1664 AgI. I = 41·40.
$C_{12}H_{21}N,HI$ requires I = 41·43 per cent.

The nitrate was prepared by adding a concentrated solution of sodium nitrate to a solution of the hydriodide.

0·1485 gave 15·0 c.c. moist nitrogen at 19° and 765 mm. N = 11·87.
$C_{12}H_{21}N,HNO_3$ requires N = 11·57 per cent.

Dimethylpinylamine.

On dissolving the hydriodide in water and adding caustic potash, the base is precipitated as a white, crystalline solid. Dimethylpinylamine crystallises from ether in small prisms which melt at 112° and which, when mixed with the unsaturated base described above, cause no depression of the melting point. Hence the identity of the two substances may be regarded as established.

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LXXXVII.—*The Reduction of* iso*Phthalic Acid. Part II.*

By WILLIAM GOODWIN and WILLIAM HENRY PERKIN, jun.

THE first part of this investigation (Perkin and Pickles, Trans., 1905, **87**, 293) dealt with the behaviour of *iso*phthalic acid on reduction with sodium amalgam; from the product, the four possible tetrahydro-*iso*phthalic acids were obtained, their properties described, and their relationship and constitutional formulæ discussed.

Attention was called to the fact that it had not been found possible to isolate, from the mixture of acids formed, even a trace of a dihydro-*iso*phthalic acid, and it was mentioned that, in this respect, *iso*phthalic acid behaves differently from phthalic and terephthalic acids, both of which, when treated with sodium amalgam, yield dihydro-derivatives as the first products of the reduction. A dihydro*iso*phthalic acid (m. p. 255°) was, however, obtained indirectly, namely, from 3 : 4-dibromohexahydro*iso*phthalic acid by the action of methyl-alcoholic potash, and to this acid the constitution $\Delta^{2 \cdot 4}$,

CO_2H / CO_2H [ring formula],

was provisionally assigned (*loc. cit.*, p. 310).*

In the present communication we describe a series of experiments having for their starting point hexahydro*iso*phthalic acid, which, as is well known, exists in *cis*- and *trans*-modifications:

[cis formula: H, CO_2H; H_2, H_2; H_2, H—CO_2H; H_2] [trans formula: CO_2H, H; H_2, H_2; H_2, H—CO_2H; H_2].

These acids were first obtained synthetically (Perkin, Trans., 1891, **59**, 808) from the product of the action of methylene di-iodide on the disodium derivative of ethyl pentanetetracarboxylate by hydrolysis and elimination of carbon dioxide. In the preparation of the considerable

* The scheme of numbering is that employed in the previous paper, that is:

[ring formula: CO_2H at 1; positions 1, 2, 3, 4, 5, 6; CO_2H at 3].

quantity of material required for the present investigation, we preferred to employ a method of synthesis which was discovered shortly afterwards (Perkin and Prentice, Trans., 1891, **59**, 990), as this appeared to be the more convenient.

In this synthesis, the disodium derivative of ethyl propanetetracarboxylate is digested with trimethylene dibromide,

$$CH_2<\begin{matrix}CNa(CO_2Et)_2\\CNa(CO_2Et)_2\end{matrix} + \begin{matrix}Br\cdot CH_2\\Br\cdot CH_2\end{matrix}>CH_2 =$$

$$CH_2<\begin{matrix}C(CO_2Et)_2\cdot CH_2\\C(CO_2Et)_2\cdot CH_2\end{matrix}>CH_2 + 2NaBr,$$

and, after hydrolysing, the hexamethylene-1 : 1 : 3 : 3-tetracarboxylic acid is heated at 180°, when it is decomposed with elimination of two molecules of carbon dioxide and formation of a mixture of the *cis*- and *trans*-modifications of hexahydro*iso*phthalic acid.

These acids cannot be separated by crystallisation, and separation has, so far, only been accomplished by taking advantage of the fact that the calcium salt of the *cis*-acid is much less soluble than that of the *trans*-acid (Trans., 1891, **59**, 808). The melting point of the *cis*-acid was given as 161—163° and that of the *trans*-acid as 120—122°. Baeyer and Villiger (*Annalen*, 1893, **276**, 255) subsequently prepared the hexahydro*iso*phthalic acids by combining the mixture of tetrahydro*iso*phthalic acids, produced when *iso*phthalic acid is reduced with sodium amalgam, with hydrogen bromide and then reducing the resulting bromohexahydro*iso*phthalic acids with zinc dust and acetic acid. The two isomerides were separated, as before, by means of their calcium salts; the less soluble calcium salt yielded the pure *cis*-acid (m. p. 161—163°), whereas the *trans*-acid was obtained from the mother liquors, and after repeated crystallisation melted at 118—120°. During the course of our experiments, we repeatedly made observations which led us to suspect that the product melting at 120°, and which had, so far, been assumed to be pure *trans*-hexahydro*iso*phthalic acid, was not a single substance.

Unlike the *cis*-modification, which crystallises in well-defined needles, the acid melting at 120° always separates in indefinite nodular masses, and the melting point is not so sharp as that which a pure substance of this nature might be expected to exhibit. The acid has, indeed, properties which are very similar to those of the curious mixture of *cis*- and *trans*-*aa*-dimethylglutaric acids (Auwers and Thorpe, *Ber.*, 1895, **28**, 623; Bone and Perkin, Trans., 1896, **59**, 268) which melts at 105—106° and cannot be separated into its components by crystallisation. The latter mixture may, however, be resolved by taking advantage of the fact that the *cis*-modification is converted into the

anhydride by the action of acetyl chloride in the cold and dissolves, whereas the *trans*-modification is unchanged by this treatment and remains undissolved. When this method was applied to the acid melting at 120°, no such separation could be accomplished, because the whole dissolved in the acetyl chloride, and on treatment with water the acid melting at 120° was recovered unchanged.

We subsequently found that this acid, when dissolved in a considerable excess of ammonia and heated for some hours with calcium chloride, yields a quantity of the calcium salt of the *cis*-acid, and, after repeating this treatment several times, the mother liquor deposits, on acidifying, pure *trans*-hexahydro*iso*phthalic acid, which crystallises from water in well-defined prismatic needles and melts at 148°.

We were now able to prepare the acid melting at 120° by mixing about equal quantities of the pure *cis*- and *trans*-modifications and crystallising the mixture from a little water; the nodular masses thus obtained melted at 120—122° and had all the properties of the substance which had previously been assumed to be pure *trans*-hexahydro*iso*phthalic acid. In the earlier experiments by Perkin and by Baeyer and Villiger (*loc. cit.*), the acid (m. p. 120°) was naturally subjected to treatment with ammonia and calcium chloride in order to show that it did not contain any of the *cis*-modification.

Perkin (*loc. cit.*, p. 814) employed a strong *neutral* solution for this purpose, and Baeyer and Villiger (*loc. cit.*, p. 261) state that they used "möglichst wenig Ammoniak," but we now find that it is necessary to have a considerable *excess* of ammonia present, otherwise no separation of the calcium salt of the *cis*-acid takes place.

In possession of this means of separation, we have prepared large quantities of the *cis*- and *trans*-modifications of hexahydro*iso*phthalic acid, and submitted these to a detailed investigation, the results of which may be briefly summarised as follows:

The *trans*-acid (m. p. 148°) is partially converted into the *cis*-acid (m. p. 163°) by heating with hydrochloric acid at 170°, and the reverse change is also true. It is clear, therefore, that if either isomeride is subjected to this treatment a condition of equilibrium is established, but the mixture, the composition of which seems to vary with the temperature and the concentration of the hydrochloric acid, has not been quantitatively investigated.

When the *trans*-acid is treated first with phosphorus pentachloride and then with bromine (1 mol.), and the product decomposed by formic acid, it yields 1-*bromo*-trans-*hexahydro*iso*phthalic acid,* which melts at 210°, and the constitution of which is proved by the fact that on reduction with zinc dust and acetic acid it is again converted into the *trans*-acid. This 1-bromo-*trans*-acid is readily decomposed by boiling

caustic potash with elimination of hydrogen bromide and formation of Δ^3-tetrahydro*iso*phthalic acid (Trans., 1905, **87**, 307),

CO_2H, CO_2H ,

but whether this acid is the direct product of the elimination of hydrogen bromide, or whether one of the other tetrahydro*iso*phthalic acids is first produced and then converted into the Δ^3-acid by the action of the caustic potash, it is impossible to say.

It is, however, interesting to note that the 1-bromo-*trans*-acid yields Δ^3-tetrahydro*iso*phthalic acid in small quantities when it is digested with dilute sodium carbonate, and since it is unlikely that this treatment would convert one modification of tetrahydro*iso*phthalic acid into another, this fact may be taken as some evidence that the Δ^3-tetrahydro-acid is the direct product of the elimination of hydrogen bromide from the bromo-*trans*-acid.*

Very little Δ^3-tetrahydro*iso*phthalic acid is, however, produced from the *trans*-bromo-acid by the action of sodium carbonate, and if the reagent is very dilute, a mere trace only is formed. The principal product of the reaction is 1-hydroxy-*trans*-hexahydro*iso*phthalic acid,

CO_2H OH, H—CO_2H ,

* By direct elimination of hydrogen bromide (without molecular change), 1-bromo-*trans*-hexahydro*iso*phthalic acid might yield either Δ^2- or Δ^3-tetrahydro*iso*phthalic acid :

CO_2H, Br—CO_2H yields CO_2H, CO_2H Δ^2. or CO_2H, CO_2H Δ^3.

and, in order to obtain evidence as to the direction in which this change takes place, the following experiment was made after the present paper had been written and was in the press. A very pure specimen of Δ^2-tetrahydro*iso*phthalic acid was prepared and boiled for half an hour with a solution of sodium carbonate (saturated at the ordinary temperature). The product was acidified and allowed to stand for 24 hours, but no trace of the very sparingly soluble Δ^3-tetrahydro*iso*phthalic acid separated, and, on extracting with ether, the whole of the Δ^2-acid was recovered unchanged. It is clear, therefore, that the latter acid does not undergo molecular change when boiled with sodium carbonate, and the obvious deduction from this experiment is, that no molecular change takes place when Δ^3-tetrahydro*iso*phthalic acid is formed from 1-bromo-*trans*-hexahydro*iso*phthalic acid by the action of alkalis.

which melts at about 160°, and when warmed with sulphuric acid at 40° is decomposed with elimination of carbon monoxide and formation of γ-ketohexahydrobenzoic acid :

$$\begin{array}{c} CO \\ / \quad \backslash \\ CH_2 \quad CH_2 \\ | \qquad\quad | \\ CH_2 \quad CH\cdot CO_2H \\ \backslash \quad / \\ CH_2 \end{array} \cdot$$

Both of these acids had already been prepared by Baeyer and Tutein (*Ber.*, 1889, **22**, 2182—2187). γ-Ketohexahydrobenzoic acid was obtained from tetrahydrohydroxyterephthalic acid (ketohexahydroterephthalic acid) by the elimination of carbon dioxide :

$$\begin{array}{c} CO \\ / \quad \backslash \\ CO_2H\cdot CH \quad CH_2 \\ | \qquad\quad | \\ CH_2 \quad CH\cdot CO_2H \\ \backslash \quad / \\ CH_2 \end{array} - CO_2 = \begin{array}{c} CO \\ / \quad \backslash \\ CH_2 \quad CH_2 \\ | \qquad\quad | \\ CH_2 \quad CH\cdot CO_2H. \\ \backslash \quad / \\ CH_2 \end{array}$$

The keto-acid was found to combine readily with hydrogen cyanide with formation of the nitrile of 1-hydroxyhexahydro*iso*phthalic acid, from which the acid itself was obtained by hydrolysis with hydrochloric acid. Baeyer and Tutein do not give the melting point of the hydroxy-acid which they prepared in this way, but, from its method of formation, it seems probable that it consisted of a mixture of the *cis*- and *trans*-modifications.

A series of experiments was next made with the object of preparing 1 : 3-dibromo-*trans*-hexahydro*iso*phthalic acid,

$$\begin{array}{c} CO_2H \quad Br \\ \backslash \;/ \\ / \quad \backslash \\ | \qquad\quad | \\ Br \!-\! CO_2H, \\ \backslash \quad / \end{array}$$

and it was found that this acid may be very readily obtained by treating *trans*-hexahydro*iso*phthalic acid first with phosphorus pentachloride and then with bromine (2 mols.), and then decomposing the product with formic acid. This acid melts at about 181°, and when digested with methyl-alcoholic potash yields a dihydro*iso*phthalic acid which is isomeric with that previously obtained from 3 : 4-dibromohexahydro*iso*phthalic acid by similar treatment (compare p. 841 ; also

Trans., 1905, **87**, 293), and the constitution of which is probably represented by the formula

$$\text{(ring with double bonds)}\ \begin{matrix}CO_2H \\ \bigcirc\ CO_2H.\end{matrix}$$

We have also investigated the action of bromine on *cis*-hexahydro*iso*phthalic acid and find that, when this acid is heated with phosphorus pentachloride and bromine at a temperature not exceeding 100°, it is converted into 1-bromo-*trans*-hexahydro*iso*phthalic acid. This conversion of a *cis*- into a *trans*-modification, under the above conditions, did not appear to have been observed until Buchner and Wedemann (*Ber.*, 1905, **38**, 1599) quite recently showed that the *cis*-modification of trimethylene-1 : 2-dicarboxylic acid, $CH_2{<}\begin{matrix}CH{\cdot}CO_2H \\ | \\ CH{\cdot}CO_2H\end{matrix}$, after being successively converted into the acid-chloride and then heated with bromine at 150—160°, yields bromo-derivatives of the *trans*-acid.

There is, however, this difference in the two series of experiments, namely, that the temperature employed by Buchner and Wedemann is much higher than that which we used in our experiments on the bromination of *cis*-hexahydro*iso*phthalic acid.

Preparation of Hexamethylene-1 : 1 : 3 : 3-*tetracarboxylic Acid and of* cis-*Hexahydro*iso*phthalic Acid.*

In the preparation of considerable quantities of these substances, the process which was found to give the best results was the following modification of the method previously employed by Perkin and Prentice (Trans., 1891, **59**, 990). Sodium (23 grams) is dissolved in alcohol (350 grams), the solution mixed with ethyl propanetetracarboxylate (166 grams) and trimethylene dibromide (101 grams), and heated in a reflux apparatus for one hour on the water-bath; and, as the action is a rather vigorous one, it is advisable, in order to avoid loss, to use a large flask and very long condenser in this operation.

The product is diluted with water, extracted with ether, and, after the ethereal solution has been well washed and dried over calcium chloride, the ether is evaporated and the residue fractionated under 25 mm. pressure. The fractions collected were:

(*a*) B. p. 120—200°. This oil evidently contained much ethyl methylenemalonate, $(CO_2Et)_2C{:}CH_2$, since it deposited a quantity of the horn-like polymeride of this substance on standing (compare Haworth and Perkin, Trans., 1898, **73**, 342; Bottomley and Perkin, Trans., 1900, **77**, 307).

(*b*) B. p. 220—240°. This fraction was a viscid, pale yellow oil and consisted largely of ethyl hexamethylenetetracarboxylate.

(*c*) B. p. 240—260°. On standing, this fraction became semi-solid owing to the separation of crystals of ethyl pentanehexacarboxylate (Bottomley and Perkin, *loc. cit.*, p. 298).*

The crude ethyl hexamethylenetetracarboxylate (which is obtained in a yield of about 35 per cent. of that theoretically possible) is hydrolysed by boiling with methyl-alcoholic potash (6 mols.) for four hours; water is then added and the solution evaporated on the water-bath with the repeated addition of small quantities of water, until the methyl alcohol has been completely removed. The concentrated solution is then acidified with hydrochloric acid and extracted at least 20 times with ether, the extracted liquor (*a*) being then treated as described below. After drying over calcium chloride, the ethereal solution is evaporated, when a pale yellow oil is obtained which gradually crystallises. The mass is left in contact with porous porcelain until free from oil, washed with a little ether, and recrystallised from warm water, when colourless, glistening crystals of hexamethylenetetracarboxylic acid separate, which melt at 217—219° and are rather sparingly soluble in cold water. The liquor (*a*) is evaporated to dryness, the residue mixed with the broken-up porous porcelain employed in the above purification and extracted with ether in a Soxhlet apparatus; the extract is mixed with the crude hexamethylenetetracarboxylic acid, obtained by the evaporation of the mother liquors from the purification of this acid and heated at 180° until carbon dioxide ceases to be evolved. The brown syrup thus obtained is digested with alcohol and sulphuric acid for 6 hours, water is then added, the ester extracted with ether in the usual way and fractionated under reduced pressure, when the greater portion distils at 160—190° (25 mm.). This is hydrolysed with methyl-alcoholic potash and, after completely removing the alcohol by evaporation with water, the acidified product is extracted 10 times with ether. The ethereal solution is carefully dried over calcium chloride and evaporated, and the residue digested for 6 hours with twice its volume of acetic anhydride and fractionated, the fraction 200—210° (30 mm.) being collected separately. The oil, which consists largely of the anhydride of *cis*-hexahydro*iso*phthalic acid and solidifies partially on cooling, is boiled with water in a reflux apparatus until dissolved, the solution

* The formation of the fractions (*a* and *c*) shows that, in the course of the above reaction, much of the ethyl propanetetracarboxylate employed must have been decomposed into formaldehyde and ethyl malonate, which then condensed to form ethyl methylenemalonate and ethyl pentanehexacarboxylate. A similar behaviour has been observed in other synthetical experiments in which the sodium derivative of ethyl propanetetracarboxylate has been employed.

is then made strongly alkaline with ammonia and heated on the water-bath with an excess of strong calcium chloride solution for some hours and until the separation of the crystalline calcium salt of the *cis*-acid appears to be complete. After collecting at the pump and washing with a little hot water, the salt is dissolved in boiling dilute hydrochloric acid, from which solution the pure *cis*-acid separates as a colourless, glistening, crystalline mass which melts at 162—163°.

Action of Heat on Hexamethylenetetracarboxylic Acid. Separation of the cis- *and* trans-*Modifications of Hexahydro*iso*phthalic Acid.*

During this investigation, about 100 grams of pure hexamethylenetetracarboxylic acid were heated at 208—210° until decomposition commenced, the temperature was then allowed to fall to 185°, and the heating continued until the evolution of carbon dioxide had completely ceased. The residue, which crystallised on cooling, was dissolved in water, made strongly alkaline with ammonia, and heated for some hours on the water-bath with strong calcium chloride solution. The crystalline calcium salt of the *cis*-acid, which separated in quantity, was collected at the pump, washed with water, and the mother liquors evaporated to a small bulk and again filtered from a further crop of crystals of the calcium salt, this operation being repeated several times in order to separate as much of this salt as possible.

From the calcium salt, the *cis*-acid is readily obtained by decomposition with hydrochloric acid and recrystallisation from water. The mother liquor of the calcium salt of the *cis*-acid is acidified, when a large quantity of a crystalline acid separates, which is collected at the pump and recrystallised from water, and in this way hard, nearly colourless, crystalline masses may be obtained which consist of pure *trans*-hexahydro*iso*phthalic acid.

0·1479 gave 0·3021 CO_2 and 0·0951 H_2O. C = 55·7 ; H = 7·2.
0·1345 „ 0·2751 CO_2 „ 0·0867 H_2O. C = 55·8 ; H = 7·1.
$C_8H_{12}O_4$ requires C = 55·8 ; H = 7·0 per cent.

trans-Hexahydro*iso*phthalic acid melts at 148°, is readily soluble in hot water and separates, on slowly cooling, in small, striated, prismatic needles.

When its solution in excess of ammonia is boiled with calcium chloride, no separation of a calcium salt takes place even after many hours.

The mother liquors of the *trans*-acid were extracted with ether and the ethereal solution evaporated, when a considerable quantity of a crystalline substance was obtained which separated from hydrochloric acid in nodular masses; this melted at 118—121° and had all the

properties of the substance previously obtained and described as *trans*-hexahydro*iso*phthalic acid (Perkin, Trans., 1891, 59, 814. Compare Baeyer and Villiger, *Annalen*, 1893, 276, 262). It is stated by the first-named author that a strong neutral solution of this acid, on the addition of calcium chloride, gives no precipitate even on continued boiling, and this is quite true. If, however, the acid is dissolved in a little water made strongly alkaline with ammonia, and heated for two hours on the water-bath with an excess of calcium chloride, a quantity of the calcium salt of the *cis*-acid gradually separates, and the mother-liquor from this deposits, on acidifying, crystals which melt at about 145° and consist of the almost pure *trans*-acid.

Equal quantities of the *cis*- and *trans*-acids were then weighed out, mixed, dissolved in a little hot water, and then allowed to crystallise slowly, when nodular masses separated which melted at 120—122° and had all the properties of the substance which was formerly supposed to be the pure *trans*-acid.

Partial Conversion of the trans-*Acid into* cis-*Hexahydro*iso*phthalic Acid by means of Hydrochloric Acid.*—*trans*-Hexahydro*iso*phthalic acid (1 gram) was heated in a sealed tube with hydrochloric acid (5 c.c.) at 170° for 1 hour, the product was extracted with ether, the ethereal solution evaporated, and the colourless, crystalline residue dissolved in excess of dilute ammonia and digested with calcium chloride. The sparingly soluble calcium salt, which soon separated, was collected, washed with warm water, and dissolved in a small quantity of boiling hydrochloric acid, from which solution the pure *cis*-acid separated in colourless needles melting at 161—162°.

0·1205 gave 0·2462 CO_2 and 0·0772 H_2O. C = 55·7; H = 7·1.
$C_8H_{12}O_4$ requires C = 55·8; H = 7·0 per cent.

From the mother liquors of the calcium salt, a small quantity of impure *trans*-acid was isolated, so that it seems probable that the conversion of this into the *cis*-acid by heating with hydrochloric acid is only partial, a result which is in harmony with previous observations on the subject.

Complete Conversion of trans-*Hexahydro*iso*phthalic Acid into the* cis-*Modification by means of Acetyl Chloride.*—*trans*-Hexahydro*iso*phthalic acid is sparingly soluble in acetyl chloride, but dissolves on warming, and, if the solution is heated at 100° for one hour and then at 150° for two hours and evaporated on the water-bath, a crystalline residue is obtained. This was left in contact with porous porcelain until quite dry and then crystallised from a mixture of benzene and light petroleum, when a satiny mass of crystals was obtained which melted at 188—189°.

0·1255 gave 0·2867 CO_2 and 0·0748 H_2O. C = 62·2; H = 6·6.
$C_8H_{10}O_3$ requires C = 62·3; H = 6·5 per cent.

That this substance was the *anhydride* of cis-*hexahydro*iso*phthalic acid* was proved by dissolving it in boiling water and concentrating the solution, when the pure *cis*-acid (m. p. 162—163°) separated on cooling. This transformation of the *trans*-modification into the *cis*-form is evidently a complete one, since no trace of *trans*-acid could be detected in the mother liquors of the *cis*-anhydride.

1-*Bromo*-trans-*hexahydro*iso*phthalic Acid.*

In preparing this acid, *trans*-hexahydro*iso*phthalic acid (3·5 grams) was heated in a tube with phosphorus pentachloride (6 grams) in the water-bath until the decomposition was complete, bromine (3·3 grams) was then added and the tube sealed and heated at 100° for two hours.

The product was mixed with twice its volume of formic acid (sp. gr. 1·22°) and allowed to remain for two days; the crystalline crust which had formed was then collected and recrystallised from formic acid.

0·1628 gave 0·2280 CO_2 and 0·0633 H_2O. C = 38·2; H = 4·3.
0·2192 „ 0·1662 AgBr. Br = 32·2.
$C_8H_{11}O_4Br$ requires C = 38·2; H = 4·4; Br = 31·9 per cent.

1-*Bromo*-trans-*hexahydro*iso*phthalic acid* melts at about 210° and separates from formic acid as a heavy powder which, under the microscope, is seen to consist of leafy masses. It is rather sparingly soluble in dry ether or cold formic acid, very sparingly so in hot benzene, toluene, light petroleum, or chloroform, but readily so in alcohol or boiling formic acid. When boiled with water, it dissolves and, if the solution is rapidly cooled, a large amount of the acid crystallises out unchanged; if, however, the solution is boiled for a few minutes, the acid is completely decomposed with elimination of hydrogen bromide and formation of a solid acid which appears to be 1-*hydroxy*-trans-*hexahydro*iso*phthalic acid* (p. 851).

Reduction.—In order to be sure that no molecular change had taken place during bromination, the above bromo-acid was dissolved in glacial acetic acid and reduced, first at the ordinary temperature and then at 100°, with a large excess of zinc dust.

The product was mixed with hydrochloric acid and distilled in steam until the acetic acid had been removed; the residue in the steam distillation flask was then extracted several times with ether, when, on evaporating the ethereal solution, a solid acid remained,

which, after crystallisation from water, melted at 143—145° and consisted of almost pure *trans*-hexahydro*iso*phthalic acid.

This result proves conclusively that the acid obtained by the bromination of this *trans*-acid under the conditions described above is 1-bromo-*trans*-hexahydro*iso*phthalic acid.

*Action of Alkalis on 1-Bromo-*trans*-hexahydro*iso*phthalic Acid. Formation of Δ^3-Tetrahydro*iso*phthalic Acid, 1-Hydroxy-*trans*-hexahydro*iso*phthalic Acid, and γ-Ketohexahydrobenzoic Acid.*

I. *Action of Caustic Potash.*—1-Bromo-*trans*-hexahydro*iso*phthalic acid dissolves readily in caustic potash, and, if the solution is boiled for a few minutes and then acidified, a sandy crystalline precipitate separates; this melts, after recrystallisation, at 242—244° and crystallises from much water in the stars with jagged edges which are so characteristic of Δ^3-tetrahydro*iso*phthalic acid (Trans., 1905, **87**, 307).

0·1618 gave 0·3360 CO_2 and 0·0880 H_2O. C = 56·6; H = 6·0.
$C_8H_{10}O_4$ requires C = 56·4; H = 5·9 per cent.

II. *Action of Sodium Carbonate.*—In studying this action, the pure bromo-acid was dissolved in an excess of dilute sodium carbonate and heated on the water-bath for 5 hours, the solution was then boiled in a reflux apparatus for half an hour, cooled, acidified, and allowed to stand for a week. A small quantity of a very sparingly soluble substance gradually separated in long, slender needles; this was collected at the pump, recrystallised from much water, and found to consist of Δ^3-tetrahydro*iso*phthalic acid.

The filtrate was saturated with ammonium sulphate, extracted five times with ether, and the ethereal solution dried over calcium chloride and evaporated, when a syrupy residue was obtained which soon completely solidified. In order to separate any trace of Δ^3-tetrahydro*iso*phthalic acid which might still be present, the whole was dissolved in a little water, boiled with animal charcoal, and evaporated to a small bulk, but, even after standing for several days, only a trace of a crystalline substance separated. The solution was now allowed to concentrate over sulphuric acid in an exhausted desiccator, when a hard, crystalline mass gradually formed; this was collected, dried at 100°, and analysed.

0·2451 gave 0·4623 CO_2 and 0·1380 H_2O. C = 51·3; H = 6·3.
$C_8H_{12}O_5$ requires C = 51·1; H = 6·4 per cent.

1-*Hydroxy*-trans-*hexahydro*iso*phthalic acid*, when purified in the manner described above, melts at about 160° with previous softening, but owing to the difficulty which was experienced in satisfactorily

recrystallising the acid, this melting point must be taken as only approximately correct. The hydroxy-acid is very soluble in water, and its solution, after neutralising with sodium carbonate, does not decolorise permanganate. The composition of this acid was further confirmed by titration with *N*/10 caustic soda, when it was found that 0·105 gram neutralised 0·044 gram NaOH, whereas this amount of a dibasic acid, $C_8H_{12}O_5$, should neutralise 0·045 gram NaOH. The *silver* salt, $C_8H_{10}Ag_2O_5$, was obtained by adding a solution of silver nitrate to a neutral solution of the ammonium salt in the form of a sparingly soluble white precipitate.

0·1351 gave 0·0722 Ag. Ag = 53·5.
$C_8H_{10}O_5Ag_2$ requires Ag = 53·7 per cent.

Baeyer and Tutein (*Ber.*, 1889, **22**, 2186), who first obtained 1-hydroxyhexahydro*iso*phthalic acid, state that it crystallises from alcohol in warty masses, but, as they do not give the melting point, it is impossible to decide whether the acid which they prepared is identical with that described above; it seems more probable from the method of formation that it was a mixture of the *cis*- and *trans*-modifications.

γ-*Ketohexahydrobenzoic Acid.*

When finely powdered 1-hydroxy-*trans*-hexahydro*iso*phthalic acid is warmed with concentrated sulphuric acid at 40°, it dissolves with evolution of carbon monoxide and without any charring. After a few minutes, and as soon as the evolution of gas had ceased, the solution was poured on to powdered ice and extracted several times with ether. After drying over calcium chloride, the ethereal solution deposited an oily acid, which was very soluble in water and yielded precipitates with phenylhydrazine and semicarbazide. In order to characterise the acid, it was dissolved in a little water and mixed with a strong solution of hydroxylamine hydrochloride, when the oxime gradually separated as a sparingly soluble crystalline powder.

0·1817 gave 14·2 c.c. nitrogen at 17° and 762 mm. N = 9·1.
$C_7H_{11}O_3N$ requires N = 8·9 per cent.

The *oxime* of γ-*ketohexahydrobenzoic acid* prepared in this way melted at about 167—168° with decomposition, whereas Baeyer and Tutein (*loc. cit.*, p. 2183) give 170° as the melting point of the specimen of this oxime, which they prepared from hydroxytetrahydroterephthalic acid by the action of hydroxylamine hydrochloride.

1 : 3-*Dibromo*-trans-*hexahydro*iso*phthalic Acid and Dihydro*iso*phthalic Acid.*

The above-mentioned dibromo-acid is readily prepared by heating *trans*-hexahydro*iso*phthalic acid (1·7 grams) with phosphorus pentachloride (2·5 grams) and then with bromine (3·5 grams) in a sealed tube at 100° for 2 hours. The oily product is poured into three times its volume of formic acid (sp. gr. 1·22), warmed at 50° until decomposition is complete, and allowed to stand for several days, when a crystalline crust will have separated. The mother liquor is decanted and left exposed to the air until no more crystals separate, the combined crops of crystals are then purified by recrystallisation from formic acid.

0·2590 gave 0·2949 AgBr. Br = 48·4.

$C_8H_{10}O_4Br_2$ requires Br = 48·5 per cent.

1 : 3-*Dibromo*-trans-*hexahydro*iso*phthalic acid* melts at about 181° and is readily soluble in ether, alcohol, or hot formic acid, but sparingly so in benzene or light petroleum. It is best crystallised from glacial formic acid, from which it separates in crusts which, under the microscope, are seen to be composed of curious oval leaflets; the separation is, however, very slow, and sometimes takes days before it is complete. The dibromo-acid is sparingly soluble in cold water, but dissolves readily on warming with decomposition and elimination of hydrogen bromide, and if the solution is boiled for a few minutes and then evaporated a viscid, syrupy acid remains which gradually crystallises. This acid, which is quite stable to permanganate, is probably 1 : 3-dihydroxy-*trans*-hexahydro*iso*phthalic acid, but it was not obtained in sufficient quantity for purification and analysis.

Action of Caustic Potash.—When the pure dibromo-acid is added to a large excess of a strong solution of pure caustic potash in methyl alcohol, a vigorous action takes place, and potassium bromide separates at once in quantity. After heating for 10 minutes on the water-bath, the product was mixed with water and boiled, out of contact with air,* until quite free from methyl alcohol; it was then cooled and acidified, when a white, crystalline precipitate separated, which closely resembled barium sulphate. This was collected, washed with water, dried at 100°, and analysed.

0·1309 gave 0·2712 CO_2 and 0·0592 H_2O. C = 56·5; H = 5·0.
0·1441 „ 0·3003 CO_2 „ 0·0643 H_2O. C = 56·8; H = 4·9.

$C_8H_8O_4$ requires C = 57·1; H = 4·8 per cent.

* If this precaution is not taken, oxidation seems to take place and *iso*phthalic acid is formed.

This *dihydroisophthalic acid* separates from acetic acid, in which it is almost insoluble in the cold and not readily so on boiling, as a crystalline powder which, under the microscope, has no characteristic appearance. It softens somewhat at 255°, but does not melt at 270°; it therefore appears to be different from the dihydro*iso*phthalic acid which was obtained from 3 : 4-dibromohexahydro*iso*phthalic acid by the action of methyl-alcoholic potash (Trans., 1905, **87**, 310), since this latter acid crystallised in stars and melted completely at 255°.

A small quantity of the dihydro*iso*phthalic acid described in the present paper was exposed over dry bromine for 3 days and then placed in an exhausted desiccator over powdered potash for 3 days. The product contained bromine, but, after crystallising from much glacial formic acid, an acid was obtained which was free from bromine and exhibited all the properties of dihydro*iso*phthalic acid, the identity with which was confirmed by analysis.

0·1212 gave 0·2506 CO_2 and 0·055 H_2O. C = 56·5; H = 5·1.
$C_8H_8O_4$ requires C = 57·1; H = 4·8 per cent.

This result seems to show that this dihydro*iso*phthalic acid is not capable of yielding an additive product when it is exposed to dry bromine vapour.

Action of Bromine on cis-*Hexahydro*iso*phthalic Acid.*

During the course of these experiments, we experienced unexpected difficulties in obtaining a definite product of bromination, although we employed the conditions which had given such good results in the case of the *trans*-acid. When the quantities taken were exactly those required for the formation of the monobromo-acid and the product was purified by repeated crystallisation from formic acid, we obtained crystalline acids melting in different experiments from 197° to 204°, and which yielded, on analysis, percentages of bromine varying from 33·2 to 35·1, whereas the formula $C_8H_{11}O_4Br$ requires 31·9 per cent. of bromine. A satisfactory result was, however, at last obtained in an experiment in which we employed a method exactly similar to that recommended by Baeyer (*Annalen*, 1888, **245**, 179) for the preparation of (I) bromohexahydroterephthalic acid.

cis-Hexahydro*iso*phthalic acid (6 grams) was digested with phosphorus pentachloride (17 grams) and then heated with bromine (6 grams) in a sealed tube at 100° for 4 hours. The product was mixed with powdered ice and left for 2 days; the sandy precipitate which had separated was collected and dissolved in 750 c.c. of cold, very dilute sodium carbonate. The solution was filtered and acidified, but, as after standing for 2 days nothing had separated, the whole

was acidified, saturated with ammonium sulphate, and extracted several times with ether. The ethereal solution was dried over calcium chloride and evaporated, when a gummy mass was obtained which gradually became semi-solid ; on warming with a little water, the gummy impurity was dissolved, leaving a white, crystalline mass.

This was collected and rapidly recrystallised from hot water, in which it is sparingly soluble, but from which it separated as a sandy, crystalline powder melting at 210°.

0·1679 gave 0·2352 CO_2 and 0·0688 H_2O. C = 38·2 ; H = 4·5.
0·1257 „ 0·0940 AgBr. Br = 31·8.
$C_8H_{11}O_4Br$ requires C = 38·2 ; H = 4·3 ; Br = 31·8 per cent.

That this substance is *bromo*-trans-*hexahydro*iso*phthalic acid* was proved by the fact that, when carefully reduced by zinc dust and acetic acid under the conditions described on p. 850, it was quantitatively converted into *trans*-hexahydro*iso*phthalic acid.

It follows, therefore, that, at some stage during the treatment with phosphorus pentachloride and bromine at 100°, transformation of the *cis*- into the *trans*-modification must have taken place.

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LXXXVIII.—*The Replacement of Hydroxyl by Bromine.*

By WILLIAM HENRY PERKIN, jun., and JOHN LIONEL SIMONSEN.

THE methods available for the preparation of aliphatic compounds in which several atoms of bromine are combined with different carbon atoms are few in number. It is usually assumed that a substance containing one or more hydroxyl groups may be converted into the corresponding bromo-derivatives by treatment with hydrobromic acid, or phosphorus tri- or penta-bromide, but in attempting to use this method in the preparation of bromo-derivatives for the purpose of ring synthesis unexpected difficulties were encountered.

The hydroxy-groups in such polyhydric alcohols as glycerol, erythritol, mannitol, &c., are usually only partially replaced by bromine when these alcohols are treated with hydrobromic acid, and if, by employing higher temperatures and a large excess of the halogen acid, the attempt is made to complete the substitution, decomposition usually takes place with much charring, and the yield obtained is consequently very small. The same remarks apply to the use of the

bromides of phosphorus in such cases, the results obtained by the action of these reagents on the polyhydric alcohols being frequently most unsatisfactory.* In investigating this matter, we found that a great improvement is achieved if the alcohol is first converted into the acetate and the latter is then heated with a solution of hydrogen bromide in glacial acetic acid (saturated at 0°) at about 150°.

By this process, which may be represented in a general way thus:

$$R{\cdot}O{\cdot}C_2H_3O + HBr = RBr + HO{\cdot}C_2H_3O,$$

the whole of the hydroxyl groups may usually be substituted by bromine, and the reaction proceeds smoothly without any separation of carbonaceous matter, consequently a good yield is obtained and the product is easily purified. We have investigated the following cases, which may serve to illustrate this process:

I. *Glycol diacetate* is converted quantitatively into ethylene dibromide, when it is heated with acetic-hydrobromic acid at 150°.

II. *Glycerol triacetate* (triacetin) is readily acted on by acetic-hydrobromic acid at 150°, and an almost quantitative yield of s-*tribromopropane*, $CH_2Br{\cdot}CHBr{\cdot}CH_2Br$, is obtained.

The behaviour of triacetin, when treated with a solution of hydrogen bromide in acetic acid, has lately also been investigated by R. de la Acena (*Compt. rend.*, 1904, **139**, 867), who found that at 0° and in the dark a monobromodiacetin is produced, whereas at 100° two acetyl groups are displaced with formation of a dibromomonacetin.

III. *Erythritol tetracetate* reacts readily with acetic-hydrobromic acid at 150°, yielding s-trans-*tetrabromobutane*, $CH_2Br{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2Br$ (m. p. 118°), and two oily substances which boil at 122—127° (26 mm.) and 164—165° (27 mm.), and which appear to consist of s-cis-*tetrabromobutane* and *erythritol tribromohydrine*, $C_4H_6Br_3{\cdot}OH$, respectively.

s-Tetrabromobutane had previously been prepared from erythritol by the action of phosphorus pentabromide (Colson, *Bull. Soc. Chim.*, 1887, **48**, 53), as well as by the following interesting indirect process.

When erythritol is heated with formic acid (Henninger, *Ann. Chim.*

* The action of hydrobromic acid on glycerol does not appear to have been investigated, but, when treated with phosphorus pentabromide, glycerol yields dibromohydrin, $CH_2Br{\cdot}CH(OH){\cdot}CH_2Br$ (Aschan, *Ber.*, 1888, **21**, 2890). When erythritol reacts with aqueous hydrobromic acid, it yields a dibromohydrin, $C_4H_6Br_2(OH)_2$, and Colson (*Bull. Soc. Chim.*, 1887, **48**, 53) found that *s.-trans*-tetrabromobutane, $CH_2Br{\cdot}CHBr_2{\cdot}CHBr{\cdot}CH_2Br$, is produced in very small quantity when erythritol is treated with phosphorus pentabromide. The action of hydrobromic acid on mannitol has been investigated by Champion (*Zeitschrift*, 1871, 348) and Bouchardat (*Ann. Chim. Phys.*, 1876, [v], **6**, 102), who showed that, when heated with a saturated aqueous solution of hydrogen bromide at 100°, it is converted into a mannitoldibromohydrin, $C_6H_8Br_2(OH)_4$.

Phys., 1886, [vi], **7**, 216), it yields erythrene, $CH_2{:}CH{\cdot}CH{:}CH_2$, a hydrocarbon which has also been prepared by passing the vapour of fusel oil through a red-hot tube (Caventou, *Annalen*, 1863, **127**, 93), and by distilling trimethylpyrrolidylammonium iodide with caustic potash (Ciamician, Magnaghi, *Ber.*, 1886, **19**, 570, and 1887, **20**, 3064). Erythrene combines readily with bromine, yielding a mixture of two isomeric tetrabromides, $C_4H_6Br_4$, which melt respectively at 118° and 39°. The former is identical with the tetrabromobutane, which we obtained from erythritol tetracetate in the manner just described. Grimaux and Cloëz (*Bull. Soc. Chim.*, 1887, **48**, 32) have shown that this substance distils at about 260—270°, and is, at the same time, partially converted into the isomeric tetrabromide melting at 39°, and in order to account for this they assume that change in constitution had taken place during distillation, and that the *s*-tetrabromobutane had been converted into a tetrabromo-compound of the formula $CH_3{\cdot}CBr_2{\cdot}CBr_2{\cdot}CH_3$. This view can hardly be accepted as correct, and it is much more probable that the two tetrabromides are *cis*- and *trans*-modifications:

$$\begin{array}{l} Br{\cdot}CH{\cdot}CH_2Br \\ \quad | \\ Br{\cdot}CH{\cdot}CH_2Br \end{array} \quad \text{and} \quad \begin{array}{l} Br{\cdot}CH_2{\cdot}C{\cdot}Br \\ \qquad\quad | \\ \qquad Br{\cdot}CH{\cdot}CH_2{\cdot}Br \end{array}$$

cis. *trans.*

and the bromide melting at 39° is probably the *cis*-modification, since it is produced from the less fusible (*trans*-)modification by the action of heat. Ciamician seems to have held a similar view of the isomerism of these tetrabromo-compounds, since he suggested in 1887 (*Ber.*, **20**, 3064) that their relationship may be of the same kind as that of the inactive modifications of dibromosuccinic and tartaric acids.

The constitution of erythrene, $CH_2{:}CH{\cdot}CH{:}CH_2$, is proved beyond doubt, not only by its method of formation from erythritol, but also by the fact that it yields *s*-tetrabromobutane when treated with bromine. This hydrocarbon contains the grouping $-C{:}C{\cdot}C{:}C-$, and its behaviour towards bromine seems therefore to make it an exception to the generalisation of Thiele (*Annalen*, 1898, **306**, 87; 1901, **319**, 129).

IV. The *tetracetate of penterythritol*, $C(CH_2{\cdot}O{\cdot}C_2H_3O)_4$, yielded interesting results, since, when heated with acetic-hydrobromic acid at 160°, it was converted into *s-tetrabromotetramethylmethane*, $C(CH_2Br)_4$, but the principal product of the reaction was *tribromotrimethylcarbinyl acetate*, $(CH_2Br)_3C{\cdot}CH_2{\cdot}O{\cdot}C_2H_3O$, one of the acetyl groups having escaped replacement by bromine.

V. In the case of *mannitol hexacetate*, it was found impossible to replace more than five of the acetyl groups by bromine, and the product of the reaction is *pentabromohexyl acetate*, $C_6H_8Br_5(O{\cdot}C_2H_3O)$,

a crystalline substance which melts at 139°. It is remarkable with what tenacity one of the acetyl groups remains, not only in this case, but also in the case just mentioned of the tetracetate of pentaerythritol.

We have also attempted to apply the method described above to the case of aromatic substances, but without success.

When phenyl acetate, $C_6H_5 \cdot O \cdot C_2H_3O$, for example, was heated with acetic-hydrobromic acid, profound decomposition set in with much charring, and no trace of bromobenzene could be isolated from the product. These negative results led us to investigate the action of phosphorus pentabromide at the ordinary temperature on the trihydric phenols, pyrogallol and phloroglucinol, but no substitution of hydroxyl by bromine could be observed. When the reaction was carried out in the presence of an indifferent solvent, such as benzene, pyrogallol yielded a *dibromopyrogallol* of the probable formula:

```
        OH
   Br/\OH
     |  |
     \/OH   ,
     Br
```

which had not previously been prepared. It melts at 150° and yields a *triacetyl* derivative, $C_6HBr_2(O \cdot C_2H_3O)_3$, melting at 143°.

Phloroglucinol, under similar conditions, is converted into tribromophloroglucinol:

```
        OH
   Br/\Br
     |  |
   OH\/OH   ,
     Br
```

which had previously been obtained by brominating phloroglucinol in acetic acid solution (Herzig, *Monatsh.*, 1885, **6**, 885).

That phosphorus pentabromide should exert such a pronounced brominating action at the ordinary temperature and in the presence of an indifferent solvent seems remarkable.

s-*Tribromopropane* (Tribromohydrin), $CH_2Br \cdot CHBr \cdot CH_2Br$.

When glycerol is digested with acetic anhydride, it is readily converted into diacetin, but even when a large excess of the anhydride is employed very little triacetin is produced (Seelig, *Ber.*, 1891, **24**, 3467; Geitel, *J. pr. Chem.*, 1898, [ii], **57**, 117). We have found that the following method may conveniently be used in preparing pure triacetin (compare Erwig and Koenigs, *Ber.*, 1889, **22**, 1464).

Glycerol (20 grams) is digested for one hour with acetic anhydride (150 grams) and zinc chloride (1 gram), the product is mixed with

ether, rapidly washed with water, dried over calcium chloride, and fractionated. Almost the whole quantity distils at 258—259° (760 mm.) and consists of pure triacetin, since a second treatment with acetic anhydride and zinc chloride does not alter the properties of the substance. Triacetin (5 grams) was now mixed with the solution of hydrogen bromide in acetic acid (28 grams) and heated in a sealed tube for 10 hours at 150—160°, the product was then poured into water and distilled in steam. The volatile oil was extracted with ether, the ethereal solution dried over calcium chloride and evaporated, when almost the whole quantity distilled at 217—219° (738 mm.) as a colourless oil which solidified in a freezing mixture and consisted of pure s-*tribromopropane*.

0·2015 gave 0·4071 AgBr. Br = 85·7.

$C_3H_5Br_3$ requires Br = 85·8 per cent.

The method just described yields a very pure product, but it is, of course, much too laborious to serve as a means of preparation, and as we required considerable quantities of tribromopropane for future experiments, we worked out the following convenient method for the preparation of this substance. Allyl bromide (100 grams) is dissolved in an equal volume of chloroform and, after cooling in a mixture of ice and salt, a solution of bromine (44 c.c.) in an equal volume of chloroform is slowly added, care being taken to keep the temperature below −5° during the operation. The chloroform is then distilled off and the tribromopropane purified by distillation under reduced pressure.

s-*Tetrabromobutane*, $CH_2Br{\cdot}CHBr{\cdot}CHBr{\cdot}CH_2Br$.

Erythritol is readily converted into its tetracetate when it is digested for a few minutes with acetic anhydride and a small piece of zinc chloride; on pouring the product into water, the tetracetate separates as a crystalline mass which, after crystallisation from acetic acid, melts at 89°. This tetracetate (20 grams) was heated in sealed tubes with the solution of hydrogen bromide in acetic acid (100 grams) for 10 hours at 160—170°, the contents of the tubes, which contained only very small quantities of carbonaceous matter, were diluted with water and distilled in steam, when a colourless oil condensed which rapidly became semi-solid. The mass was collected at the pump, washed with water, and left in contact with porous porcelain until quite free from oil; it was then crystallised from glacial acetic acid.

The crystalline mass, which was obtained in a yield of 15 grams, melted at 118—119°, and consisted of s-trans-*tetrabromobutane*, as the following analysis shows:

0·1408 gave 0·2815 AgBr. Br = 85·1.

$C_4H_6Br_4$ requires Br = 85·5 per cent.

A considerable quantity of this tetrabromo-compound was submitted to distillation under reduced pressure, when it was found that almost the whole passed over at 130—135° (30 mm.) with scarcely any decomposition. No transformation of the *trans*- into the *cis*-modification had taken place during distillation (compare p. 857), as was shown by the fact that the product, when fractionally crystallised from light petroleum, yielded nothing but the tetrabromo-compound melting at 118—119°.

When the aqueous liquors from the distillation in steam (see above) were extracted with ether, a considerable quantity of a viscid oil was obtained; this was added to the ethereal extract of the porous porcelain used in the purification of the crude tetrabromobutane and fractionated under reduced pressure. It was thus separated into a heavy, mobile oil boiling at 122—127° (26 mm.), and a viscid, syrupy substance which distilled at 164—165° (27 mm.).

The former evidently consisted, for the most part, of the *cis*-modification of tetrabromobutane, although the analytical numbers (Br = 83·6 instead of 85·5) were not very satisfactory. The oil boiling at 164—165° (27 mm.) is probably the tribromohydrin of erythritol; but we were not successful in obtaining it in a state of purity.

0·1473 gave 0·0784 CO_2 and 0·0256 H_2O. C = 14·5; H = 2·0.
0·2445 gave 0·4544 AgBr. Br = 79·0.
$C_4H_7OBr_3$ requires C = 15·4; H = 2·2; Br = 77·1 per cent.

s-*Tetrabromotetramethylmethane*, $C(CH_2Br)_4$, and *Tribromotrimethylcarbinyl acetate*, $(CH_2Br)_3C{\cdot}CH_2{\cdot}O{\cdot}C_2H_3O$.

The penterythritol employed in these experiments was prepared by the condensation of formaldehyde with acetaldehyde in the presence of milk of lime exactly according to the instructions of Tollens and Wigand (*Annalen*, 1891, **265**, 319).* In order to obtain the tetracetyl derivative, the alcohol (20 grams) was digested with acetic anhydride (75 grams) and a small piece of zinc chloride, when a vigorous reaction set in and, after boiling for two hours, the product was cooled and shaken with three times its volume of water.

The tetracetate, which separated in voluminous needles, is in this form sufficiently pure for the experiments described in this paper; it crystallises readily from alcohol in glistening needles and melts at 84—86°. Tollens and Wigand (*loc. cit.*, p. 327), who prepared the same acetate from penterythritol by the action of sodium acetate and acetate anhydride, give the same melting point, and they proved by a

* We are much indebted to Prof. W. J. Pope for a large supply of this valuable material.

direct determination of the acetyl groups that the substance is tetracetylpenterythritol. In investigating the behaviour of this substance towards hydrogen bromide, it was heated, in quantities of 5 grams, with the solution of hydrogen bromide in acetic acid (50 grams), in which it readily dissolves, in a sealed tube at 160° for 8 hours.

Very little discoloration had taken place and the tube was filled with crystals; after pouring into water, the mass was collected at the pump, washed with water, and crystallised from glacial acetic acid, from which s *tetrabromotetramethylmethane* separated in glistening, leafy masses.

0·2062 gave 0·3998 AgBr. Br = 82·6.
$C_5H_8Br_4$ requires Br = 82·5 per cent.

This interesting substance had already been obtained by Rave and Tollens (*Annalen*, 1893, **276**, 61) by the action of phosphorus tribromide on penterythritol, and these authors state that it melts at 154—156°; but, after repeated recrystallisation from acetic acid, we found that the correct melting point was 158°. One of the most characteristic properties of the tetrabromide is the fact that it is very sparingly soluble in the usual solvents; it is, however, moderately soluble in boiling toluene or glacial acetic acid.*

The acetic acid mother liquors from the purification of the tetrabromide yield, on dilution with water, an oil which soon becomes semisolid, and if this is left in contact with porous porcelain until the oily impurity is absorbed, a colourless mass remains which, on crystallisation from light petroleum, is readily separated into small quantities of tetrabromotetramethylmethane and into *tribromotrimethylcarbinyl acetate*. After repeated crystallisation from light petroleum (b. p. 60—70°) this latter substance yielded the following results on analysis:

0·1922 gave 0·1568 CO_2 and 0·0519 H_2O. C = 22·3; H = 3·0.
0·1748 ,, 0·2689 AgBr. Br = 65·4.
0·1638 ,, 0·2522 AgBr. Br = 65·5.
$C_7H_{11}O_2Br_3$ requires C = 22·8; H = 3·0; Br = 65·4 per cent.

Tribromotrimethylcarbinyl acetate separates in large, glistening prisms

* A number of experiments on the action of *s-trans*-tetrabromotetramethylmethane on the sodium derivatives of ethyl malonate, cyanoacetate, &c., were instituted, as very interesting results might be expected from the study of such reactions. The decomposition was, however, in each case most incomplete, and definite products could not be obtained in sufficient quantity for investigation. These negative results seem to be due partly to the fact that *s*-tetrabromotetramethylmethane is very sparingly soluble and partly to its unexpectedly stable nature.

The reactions were carried out in the presence of various solvents, but, even when a large excess of the sodium derivative was employed, much of the tetrabromotetramethylmethane was always recovered from the product of the reaction.

resembling sugar crystals when its solution in light petroleum is allowed to slowly evaporate in the air. It melts at 44—45°, and, unlike tetrabromotetramethylmethane, is readily soluble in most organic solvents.

Pentabromohexyl Acetate, $C_6H_8Br_5(O\cdot C_2H_3O)$.

The mannitol hexacetate required in these experiments was prepared by heating mannitol (20 grams) with acetic anhydride (100 grams) and zinc chloride (1 gram) in a reflux apparatus for one hour.

On pouring the cold product into water, the hexacetate was precipitated as a crystalline solid and purified by recrystallisation from acetic acid, from which it separated in colourless needles of melting point 121—122°. In investigating the action of hydrogen bromide, the acetate (4 grams) was mixed with the saturated solution of hydrogen bromide in acetic acid (28 grams) and heated in a sealed tube in boiling water for one day and then for 10 hours at 130—140°.

The product, which contained only a trace of carbonaceous matter, was poured into much water, when a heavy oil separated; this was extracted with ether, the ethereal solution washed with water and then with sodium carbonate, dried over calcium chloride, evaporated, and the residue repeatedly extracted with boiling light petroleum.

After filtering and evaporating, a pale yellow oil was obtained which, over sulphuric acid in an exhausted desiccator, gradually became semi-solid and, in contact with porous porcelain, the oily impurity was soon removed, leaving an almost colourless mass of crystals. From light petroleum, the substance separates in stars and, after twice recrystallising, the following results were obtained on analysis:

0·1829 gave 0·1213 CO_2 and 0·0328 H_2O. C = 18·0; H = 2·0.
0·1611 ,, 0·2806 AgBr. Br = 74·1.
0·1864 ,, 0·3262 AgBr. Br = 74·4.
$C_8H_{11}Br_5O_2$ requires C = 17·8; H = 2·0; Br = 74·2 per cent.

Pentabromohexyl acetate melts at 138—139°.

Several attempts were made to convert this substance into hexabromohexane, $CH_2Br(CHBr)_4CH_2Br$, by the removal of the remaining acetyl group, but without success. In one experiment, the pentabromo-compound was heated with a very large excess of the solution of hydrogen bromide in acetic acid at 150—160° for 8 hours. The clear, pale yellow solution was poured into water, when a solid, crystalline substance separated, which was found to be unchanged pentabromohexyl acetate.

Dibromopyrogallol, $C_6HBr_2(OH)_3$.

This substance is produced when pyrogallol (14 grams) is suspended in benzene (250 c.c.) and allowed to react, at the ordinary temperature, with phosphorus pentabromide (100 grams). Hydrogen bromide is evolved in quantity and, if after 24 hours the whole is shaken with water, a white solid separates. This is collected at the pump, mixed with a small quantity of the same substance which is obtained by evaporating the benzene solution, and the whole purified by recrystallisation from water.

0·2503 gave 0·2344 CO_2 and 0·0359 H_2O. C = 25·5 ; H = 1·6.
0·1554 „ 0·2057 AgBr. Br = 56·3.
$C_6H_4O_3Br_2$ requires C = 25·3 ; H = 1·4 ; Br = 56·3 per cent.

Dibromopyrogallol does not appear to have been previously prepared. It is a colourless, crystalline substance which melts at 150° and is readily soluble in hot water or alcohol, but only sparingly so in benzene or light petroleum. It dissolves readily in caustic alkalis, yielding solutions which rapidly become brown in contact with the air.

Triacetyldibromopyrogallol, $C_6HBr_2(O{\cdot}C_2H_3O)_3$.—This acetyl compound is readily obtained by digesting dibromopyrogallol (3 grams) for one hour with acetic anhydride (20 grams) and a small piece of zinc chloride. The cold product is mixed with water, the solid which separates collected on the pump and purified by recrystallisation from acetic acid.

0·1726 gave 0·2226 CO_2 and 0·0401 H_2O. C = 35·1 ; H = 2·4.
0·1931 „ 0·1791 AgBr. Br = 39·4.
$C_{12}H_{10}O_6Br_2$ requires C = 35·1 ; H = 2·5 ; Br = 39·0 per cent.

Triacetyldibromopyrogallol separates from acetic acid in glistening plates and melts at 143°.

Tribromophloroglucinol, $C_6Br_3(OH)_3$.

The phloroglucinol used in these experiments was first dried at 110—120°, in order to remove the water of crystallisation, and the anhydrous substance (14 grams) suspended in benzene was mixed with phosphorus pentabromide (100 grams) and allowed to stand at the ordinary temperature for 24 hours. The mixture was poured into water, and the solid which separated collected at the pump and purified by recrystallisation from water. The brownish needles thus obtained contained water of crystallisation, which was removed by drying at 100—110°. The anhydrous substance melted at 149—150°, and gave the following results on analysis :

0·1912 gave 0·1396 CO_2 and 0·0202 H_2O. C = 19·9; H = 1·1.
$C_6H_3O_3Br_3$ requires C = 19·9; H = 0·8 per cent.

There can be no doubt that this substance is *tribromophloroglucinol*, since the triacetyl compound, prepared by means of acetic anhydride and zinc chloride, melted at 180—183°, whereas Herzig (*Monatsh.*, 1885, **6**, 887) gives the melting point of this substance as 181—183°.

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LXXXIX.—*The Ethereal Salts and Amide of Dimethoxy-propionic Acid derived from* d-*Glyceric Acid.*

By PERCY FARADAY FRANKLAND and NORMAN LESLIE GEBHARD, M.Sc.

IN a number of previous communications by one of us it has been shown how the optical activity of *d*-glyceric acid is affected by the substitution of:

(1) Its carboxylic hydrogen by methyl, ethyl, propyl, butyl, &c. (ethereal salts of *d*-glyceric acid).

(2) The two hydroxylic hydrogen atoms in the above ethereal salts by the acetyl, propionyl, benzoyl, toluyl, phenacetyl, and chloro-acetyl radicles (ethereal salts of diacidyl glyceric acids).

(3) The carboxylic hydroxyl by the amido-, anilido-, &c., groups (amide, anilide, &c., of *d*-glyceric acid).

The present communication deals with the effect on rotation of the substitution by two methyl groups of the two hydroxylic hydrogen atoms in the ethereal salts of *d*-glyceric acid (ethereal salts of dimethoxypropionic acid), together with an account of the amide and methylamide of dimethoxypropionic acid.

These substitutions were effected by taking advantage of the elegant method of alkylation discovered and elaborated by Purdie and his pupils (Trans., 1899, **75**, 153 and 483), in which the ester of the hydroxy-acid is acted upon by alkyl iodide in the presence of silver oxide. This reaction is of the very greatest value in alkylating optically active hydroxy-acids, inasmuch as it has been shown by these investigators that no racemisation takes place in the process.

By the alkylation of the ethereal salts of *d*-glyceric acid, the optical activity (lævorotation) is in all cases greatly increased without change of sign, and this increase effected by alkylation is much more

pronounced than that effected by the corresponding process of acetylation, thus :

Molecular Rotation, $[M]_D^{15°}$.

	Glycerate.	Increase in rotation due to acetylation.	Diacetyl-glycerate.	Increase in rotation due to methylation.	Dimethoxy-propionate.
Methyl	−5·76°	18·80°	−24·56°	98·0°	−103·8°
Ethyl	12·30	23·26	35·56	102·1	114·4
Propyl	19·15	26·02	45·17	103·3	122·5
*iso*Propyl	17·49	24·20	41·69	—	—
n-Butyl	21·37	—	—	102·8	124·2
*iso*Butyl	23·05	27·33	50·38	—	—
sec.-Amyl (butylmethyl).	24·85	25·69	50·54	—	—
n-Heptyl	23·05	24·84	47·89	104·8	127·9
n-Octyl	22·28	25·64	47·92	103·3	125·6

From the above it will be seen that, both in the case of acetylation and of alkylation, the increase in molecular rotation is remarkably constant throughout the series of esters from the ethyl term upwards. As in the case of practically all the other physical constants of homologous series, the methyl term is exceptional, and both by acetylation and alkylation the increment in the molecular rotation of the methyl ester is distinctly less than in the case of the higher esters.

Considering only the esters of the normal alcohol radicles, it will be observed that both in the glycerates and in the dimethoxypropionates the maximum molecular rotation is reached in the case of the heptyl term,* whilst in the case of the diacetylglycerates the heptyl and octyl esters are practically of identical molecular rotation, so that there is no evidence of a maximum having been attained in this series.

It is noticeable, also, that in the normal dimethoxypropionates, as in the other normal series, the further increments in molecular rotation, after the propyl term has been reached, are comparatively small. This phenomenon serves to emphasise what has already been pointed out by one of us, that inasmuch as on stereochemical grounds it is believed that "a continuous chain of five carbon atoms will all but return upon itself, and beyond this further additions to the chain will lead to such interference as must necessitate a readjustment of the exact positions occupied by the carbon atoms in a shorter chain . . . . this stereochemical change should be betrayed by some irregularity in the rotatory manifestations."

* Of course, the maximum *may* be attained at the pentyl or hexyl term, the rotation of these esters being still unknown.

The anticipated "irregularity" is in all the three normal series referred to above recognisable in the greatly diminished rate of increase in the molecular rotation which takes place after the propyl term has been reached.

The rotations have in all cases been determined over a wide range of temperature from 15—97°, and with rise of temperature a diminution in the rotation invariably takes place, whilst in the case of the glycerates and diacetylglycerates it has been previously shown that the rotation increases with rise of temperature.

In view of the great similarity between the structure of the lactates and glycerates, it is interesting to compare the molecular rotations of these on the one hand, and of their correspondingly alkylated derivatives on the other; thus the following figures are given by Purdie and Irvine (Trans., 1899, **75**, 487):

	Lactates, $[M]_D^{20°}$.	Effect of alkylation on molecular rotation.	Mono-methoxy-propionates, $[M]_D^{20°}$.
Methyl	−8·6°	−104·1°	−112·7°
Ethyl............	−12·2	−106·7	−118·9
			Mono-ethoxy-propionates.
Methyl	−8·6°	−99·1°	−107·7°
Ethyl............	−12·2	−104·2	−116·4
		Effect of acetylation.	Acetyl-lactates.*
Ethyl............	−12·2°	−67·5°	−79·7°

* Purdie and Williamson, Trans., 1896, **69**, 830.

On comparing these figures with those in the previous table referring to the glycerates and their derivatives, it will be seen that not only have the lactates and glycerates very similar rotations, but the mono- and di-methoxypropionates are also very similar in rotatory power, the groups CH_3– and $CH_3{\cdot}O{\cdot}CH_2$– having apparently very similar rotatory effects when they are directly united to the asymmetric carbon atom. On the other hand, there is a very great difference between the rotations of ethyl acetyl-lactate and ethyl diacetylglycerate.

This difference between the rotatory effects of the alkyloxy- and the acyloxy-groups has already been pointed out by Purdie and Irvine (Trans., 1901, **79**, 964) in respect of ethyl malate, ethyl monomethoxysuccinate, and ethyl acetylmalate, on the one hand, and of ethyl tartrate, ethyl dimethoxysuccinate, and ethyl diacetyltartrate on the other. In fact, the relationship between the constitution of the lactates and the glycerates is very similar to that subsisting between the malates and the tartrates, and in the following tables the molecular rotations of the several lactic and malic derivatives are compared with those of the corresponding glyceric and tartaric derivatives:

Methyl Esters.

Lactates and derivatives.	$t°$.	$[M]_D$.	Glycerates and derivatives.	$t°$.	$[M]_D$.
Methyl lactate	20°	−8·6°	Methyl glycerate	15°	−5·8°
,, acetyl-lactate	16·5	−76·4 *	,, diacetylglycerate .	15	−24·6
			,, dipropionylglycerate	15	−25·5
			,, di-monochloroacetylglycerate...	15	−35·2
			,, di-dichloroacetylglycerate	15	−47·7
			,, di-phenacetylglycerate	14·5	−57·2
			,, di-trichloroacetylglycerate	12	−58·2
,, methoxypropionate	20	−112·7	,, di-methoxypropionate	15	−103·8
,, ethoxypropionate...	20	−107·7			
			,, di-*o*-toluylglycerate	20	+71·9
			,, di-benzoylglycerate	20	+87·5
			,, di-*m*-toluylglycerate	20	+94·0
			,, di-*p*-toluylglycerate	20	+146·7

* Calculated from the value given by P. Frankland and Henderson, see footnote in next table.

Ethyl Esters.

Lactates and derivatives.	$t°$.	$[M]_D$.	Glycerates and derivatives.	$t°$.	$[M]_D$.
Ethyl lactate	20°	−12·2°	Ethyl glycerate	15°	−12·3°
,, acetyl-lactate	20	−79·7	,, diacetylglycerate ..	15	−35·6
			,, di-monochloroacetylglycerate ...	15	−48·2
			,, di-dichloroacetylglycerate	16·8	−65·3
			,, di-trichloroacetylglycerate	12·5	−79·3
,, methoxypropionate .	20	−118·9	,, di-methoxypropionate	15	−114·4
,, ethoxypropionate ...	20	−116·4			
			,, di-*o*-toluylglycerate.	20	+80·1
,, benzoyl-lactate	15	+59·0 *	,, di-benzoylglycerate.	20	+89·2
			,, di-*m*-toluylglycerate	20	+99·5
			,, di-*p*-toluylglycerate	20	+156·9

* This figure is calculated from the value given by P. Frankland and Henderson (Proc., 1895, **11**, 54); making allowance for the partial inactivity of their material, a similar calculation made for ethyl acetyl-lactate gave $[M]_D$ −79·4°, whilst Purdie and Williamson (Trans., 1896, **69**, 830), using pure material, found −79·7°. Hence, the calculated values for ethyl benzoyl-lactate in this table and for methyl acetyl-lactate in the previous table are probably substantially correct.

Methyl Esters.

Malates and derivatives.	t°.	[M]ᴅ.	Tartrates and derivatives.	t°.	[M]ᴅ/2.*
Methyl malate	20°	−11·1°	Methyl tartrate	20°	+1·9°
,, acetylmalate	20	−46·8	,, dipropionyltartrate	15	−15·5
,, propionylmalate	20	−50·0	,, dibutyryltartrate	13	−24·0
,, butyrylmalate	20	−52·1	,, dimonochloroacetyltartrate	20	−1·1
			,, didichloroacetyltartrate	20	+23·8
			,, diphenylacetyltartrate	18	+30·0
,, benzoylmalate	21	−15·0	,, dibenzoyltartrate	100	−140·1
,, o toluylmalate	23	−25·0	,, di-o-toluyltartrate	100	−140·8
			,, ,, ,,	19	−162·4
,, m-toluylmalate	20	−17·8	,, di-m-toluyltartrate	100	−163·6
,, p-toluylmalate	18·5	−8·8	,, di-p-toluyltartrate	100	−212·9
			,, di-o-nitrobenzoyltartrate	100	−233·2
			,, di-m-nitrobenzoyltartrate	100	−164·8
			,, di-m-nitrobenzoyltartrate	22	−188·9
			,, di-p-nitrobenzoyltartrate	100	−256·0
,, methoxysuccinate	12	−92·4	,, di-methoxysuccinate	60	+85·0 †
,, ethoxysuccinate	19	−115·9			

* In the case of the tartrates, the molecular rotation has been halved in order to exhibit that which is due to the single asymmetric carbon atom.

† At 20°, the molecular rotation [M]ᴅ/2 would probably be about +90°.

Ethyl Esters.

Malates and derivatives.	t°.	[M]ᴅ.	Tartrates and derivatives.	t°.	[M]ᴅ/2.
Ethyl malate	20°	−19·8°	Ethyl tartrate	20°	+7·9°
,, acetylmalate	20	−52·3	,, diacetyltartrate	20	+5·0
,, propionylmalate	20	−54·6	,, dipropionyltartrate	16	+0·6
,, butyrylmalate	20	−57·8	,, dibutyryltartrate	16	−1·4
			,, di-monochloroacetyltartrate	15·5	+13·3
			,, di-dichloroacetyltartrate	16	+34·9
			,, di-phenacetyltartrate	20	+39·6
			,, ,, ,,	100	+20·0
,, benzoylmalate	21	−11·4	,, di-benzoyltartrate	20	−123·6
			,, ,, ,,	100	−125·8
,, o-toluylmalate	21	−19·3	,, di-o-toluyltartrate	30	−133·4
			,, ,, ,,	100	−121·0
,, m-toluylmalate	21	−14·4	,, di-m-toluyltartrate	20·5	−153·2
			,, ,, ,,	100	−140·9

Ethyl Esters (continued).

Malates and derivatives.	$t°$.	$[M]_D$.	Tartrates and derivatives.	$t°$.	$[M]_D/2$.
Ethyl *p*-toluylmalate.........	20°	−0·7°	Ethyl di-*p*-toluyltartrate ..	20°	−242·2°
			,, ,, ,,	100	−198·9
			,, di-pyromucyl-tartrate	20	−160·7
			,, di-*o*-nitrobenzoyl-tartrate	15	−332·3
			,, ,, ,,	100	−157·9
			,, di-*m*-nitrobenzoyl-tartrate	20	−178·7
			,, ,, ,,	100	−162·2
			,, di-*p*-nitrobenzoyl-tartrate	13	−325·9
			,, ,, ,,	99	−245·9
,, methoxysuccinate ...	18	−102·2	,, di-methoxysuccinate	20	+105·3
,, ethoxysuccinate	17	−121·0	,, di-ethoxysuccinate..	18	+122·1

Dimethoxypropionic Amide and Methylamide.

We have added to the number of known optically active amides by the preparation of two new representatives of this class—dimethoxypropionamide and dimethoxypropionic methylamide. The amide has had its rotation determined in water and in pyridine, the methylamide in methyl alcohol solution.

In the following table, the rotations of these compounds are compared with those of some closely allied amides:

	Solvent.	p, per cent. solution.	$t°$.	$[M]_D$.
Glyceramide	Liquid	—	20°	−46·4°
,, ...	Methyl alcohol	2·4390	20	−66·2
,, ...	,,	4·7619	20	−64·9
Dimethoxypropionamide	,,	1·6026	20	−72·4
,, ...	,,	3·1283	20	−72·6
Dimethoxypropionic methylamide..	,,	1·0520	20	−87·2
,, ,, ..	,,	1·8918	20	−86·3
Malamide	Water	c=4·32	20	−49·6
,, ...	,,	c=8·65	20	−50·2
				$[M]_D/2$.*
Tartramide	,,	0·077	20	+80·0°
,, ...	,,	1·305	20	+79·0
Tartaric methylamide................ ..	,,	0·994	20	+127·5
,, ,, ...	,,	10·35	20	+121·0
				$[M]_D/2$.*
Dimethoxysuccinamide	,,	c= 0·72	20	+83·1°†
,, ...	,,	(not given)	20	+93·2 †

* As in the previous tables (p. 868 and above), the molecular rotations of the tartaric derivatives have been halved in order to exhibit the rotation due to a single asymmetric carbon atom.

† Both these values are given by Purdie and Irvine (Trans., 1901, **79**, 960), who, however, suggest that the higher one is above the truth owing to the probable presence of a small quantity of some more active product.

From the above it will be seen that the molecular rotations exhibit the following relationships :

Glyceramide $<$ dimethoxypropionamide $<$ dimethoxypropionic methylamide (all three in methyl alcohol solution) ; similarly
Tartramide $<$ dimethoxysuccinamide (both in water solution), and
Tartramide $<$ tartaric methylamide (both in water solution), and
Malamide $<$ tartramide (both in water solution).

Experimental.

The dimethoxypropionates were in all cases prepared by the methylation of the corresponding glyceric esters, the latter being obtained by heating active glyceric acid with the alcohol in a sealed tube as described by P. Frankland and MacGregor (Trans., 1893, **63**, 511, 1410).

Methyl Dimethoxypropionate.

The methyl glycerate employed exhibited a rotation

$$a_D - 6{\cdot}44°,\ l = 1,\ t = 20°,$$

whilst Frankland and MacGregor (*loc. cit.*) found

$$a_D - 6{\cdot}15°,\ l = 1,\ t = 15°.$$

Twenty-four grams of methyl glycerate (1 mol.), together with methyl iodide (6 mols.), were dissolved in ether, and to this silver oxide (3 mols.) was added, the vigorous reaction which ensued being moderated by cooling. Subsequently the mixture was heated for four hours on the water-bath, filtered, and the residue repeatedly extracted with ether. The ethereal solution was dried over anhydrous sodium sulphate, and, after driving off the ether, distillation in a vacuum yielded a principal fraction (13 grams) between 75° and 80° under 15 mm. pressure (temp. of oil-bath, 90°). The rotation was

$$a_D - 74{\cdot}00°,\ l = 1,\ t = 20°.$$

This product was washed with water to remove any unaltered methyl glycerate, as well as any of the mono-methoxy-derivative which might have been formed, and after drying and distilling twice again, the rotation and boiling point (77—78° under 15 mm.) were practically unaltered :

$$a_D - 37{\cdot}00°,\ l = 0{\cdot}4992,\ d\ 20°/4° = 1{\cdot}0634.$$
$$[a]_D^{20°} - 69{\cdot}70°\ ;\ [M]_D^{20°} - 103{\cdot}16°.$$

The ester is somewhat soluble in cold water, from which it separates on warming.

0·1536 gave 0·2749 CO_2 and 0·1110 H_2O. C = 48·81 ; H = 8·03.
0·1613 ,, 0·2875 CO_2 ,, 0·1185 H_2O. C = 48·61 ; H = 8·16.
Calculated for $C_6H_{12}O_4$, C = 48·65 ; H = 8·11 per cent.

Ethyl Dimethoxypropionate.

The ethyl glycerate used for this preparation exhibited a rotation

$$\alpha_D - 10·94°,\ l = 1,\ t = 20°,$$

whilst Frankland and MacGregor (*loc. cit.*) give

$$\alpha_D - 10·85°,\ l = 1,\ t = 15°.$$

23·7 grams of this ester were methylated as above; the reaction, being extremely vigorous, had to be repeatedly moderated by cooling. The crude product distilled from the ether extract amounted to 12 grams, and passed over at 85–90° (17 mm.; oil-bath, 110°); α_D – 36·05°, l = 0·4992, t = 20°. The rotation was not affected by two subsequent redistillations; the boiling point of the final product (7·5 grams) was 92° (17 mm.; oil-bath, 115°).

I. 0·1000 gave 0·1890 CO_2 and 0·0782 H_2O. C = 51·55; H = 8·69.
II. 0·1283 ,, 0·2436 CO_2 ,, 0·0997 H_2O. C = 51·78; H = 8·63.
Calculated for $C_7H_{14}O_4$, C = 51·85 ; H = 8·64 per cent.

$$\alpha_D - 36·00°,\ l = 0·4992,\ t = 20°,\ d\ 20°/4° = 1·0309.$$
$$[\alpha]_D^{20°} - 69·95° ;\ [M]_D^{20°} - 113·32°.$$

Propyl Dimethoxypropionate.

The propyl glycerate employed was found to have a rotation α_D – 14·5°, l = 1, t = 20°, as compared with that observed by Frankland and MacGregor (*loc. cit.*), α_D – 14·7°, l = 1, t = 17°. The reaction in methylating was again vigorous.

From 20 grams of propyl glycerate, 10·5 grams of a faintly yellow liquid distilling at 90—100° (15 mm.; oil-bath at 110—115°) were obtained. It had a rotation α_D – 34·70°, l = 0·4992, t = 20°. The latter was practically unaffected by two further redistillations, the boiling point of the final product (7·3 grams) being 93—95° (15 mm.; oil-bath at 115°).

I. 0·1558 gave 0·3125 CO_2 and 0·1285 H_2O. C = 54·70; H = 9·16.
II. 0·1428 ,, 0·2855 CO_2 ,, 0·1158 H_2O. C = 54·53; H = 9·01.
Calculated for $C_8H_{16}O_4$, C = 54·54 ; H = 9·09 per cent.

$$\alpha_D - 34·76°,\ l = 0·4992,\ t = 20°,\ d\ 20°/4° = 1·0090.$$
$$[\alpha]_D^{20°}\ - 69·01° ;\ [M]_D^{20°}\ - 121·46°.$$

Butyl Dimethoxypropionate.

The butyl glycerate used exhibited a rotation α_D $-7{\cdot}03°$, $l=0{\cdot}4992$, $t=20°$, as compared with Frankland and MacGregor's value of α_D $-14{\cdot}50°$, $l=0{\cdot}992$, $t=17°$. The reaction, on methylating, appeared to be more violent than in the previous cases, doubtless owing to the butyl glycerate being more soluble in methyl iodide, whilst in the case of methyl and ethyl glycerate, complete solution in the methyl iodide could only be brought about by the addition of ether, and it has been shown by Lander (Trans., 1900, 77, 729) that the Purdie reaction is only applicable to substances soluble in the alkyl iodide or soluble with the latter in a common solvent. After the reaction had abated, the mixture was heated for one hour on the water-bath, the products separating into two layers. After extracting with ether and drying, there were obtained from 28 grams of butyl glycerate 17 grams of a colourless liquid distilling at 109—114° (15 mm.; oil-bath, 135°), and of rotation α_D $-32{\cdot}11°$, $l=0{\cdot}4992$, $t=20°$.

Washing with water and redistilling twice did not affect the rotation. The final product (12 grams) distilled at 114—115° (15 mm.; oil-bath, 135°).

I. 0·1353 gave 0·2833 CO_2 and 0·1154 H_2O. C = 57·11; H = 9·48.
II. 0·1451 ,, 0·3040 CO_2 ,, 0·1238 H_2O. C = 57·14; H = 9·48.
Calculated for $C_9H_{18}O_4$, C = 56·84; H = 9·47 per cent.

$$\alpha_D - 32{\cdot}13°,\ l=0{\cdot}4992,\ t=20°,\ d\ 20°/4°=0{\cdot}9921.$$
$$[\alpha]_D^{20°}\ -64{\cdot}88°;\ [M]_D^{20}\ -123{\cdot}27°.$$

Heptyl Dimethoxypropionate.

The heptyl glycerate * employed had a rotation of α $-5{\cdot}03°$, $l=0{\cdot}4992$, $t=20°$, whilst Frankland and MacGregor found $\alpha_D - 11{\cdot}65°$, $l=0{\cdot}992$, $t=18°$. As in all the previous cases it had been found possible to confirm Frankland and MacGregor's figures by the repeated fractionation of our products, we deemed it unnecessary on this occasion to resort to the complete purification of the ester, as much loss is, of course, thereby entailed, and it is therefore more advantageous to rely on the purification after methylation.

The violence of the reaction in methylating was moderated by mixing a large volume of pure ether with the heptyl glycerate and silver oxide, the methyl iodide being then gradually added drop by drop. After the visible action had ceased, the whole was heated for one hour on the water-bath.

* Prepared from a heptyl alcohol boiling at 176—178° and proved to be inactive.

From 20 grams of heptyl glycerate, 13 grams of a colourless liquid distilled over at 142—148° (15 mm. ; oil-bath, 170°). This was found to have a rotation of $\alpha_D - 26{\cdot}33°$, $l = 0{\cdot}4992$, $t = 20°$.

After washing with water, drying, and again twice distilling, the final product (9 grams) passed over at 144—146° (15 mm. ; oil-bath, 170°).

I. 0·1497 gave 0·3397 CO_2 and 0·1370 H_2O. C = 61·89 ; H = 10·17.
II. 0·1464 „ 0·3318 CO_2 „ 0·1360 H_2O. C = 61·81 ; H = 10·32.
Calculated for $C_{12}H_{24}O_4$, C = 62·07 ; H = 10·34 per cent.

$\alpha_D - 26{\cdot}20°$, $l = 0{\cdot}4992$, $t = 20°$, $d\ 20°/4° = 0{\cdot}9571$.
$[\alpha]_D^{20°} - 54{\cdot}84°$; $[M]_D^{20°} - 127{\cdot}23°$.

Octyl Dimethoxypropionate.

The octyl glycerate exhibited the rotation $\alpha_D - 5{\cdot}05°$, $l = 0{\cdot}4992$, $t = 20°$, closely corresponding to Frankland and MacGregor's value of $\alpha_D - 10{\cdot}40°$, $l = 0{\cdot}992$, $t = 19°$. The methylation was carried out in exactly the same manner as with the heptyl ester. From 20 grams of octyl glycerate there were obtained 11 grams of crude product; this was very yellow, distilled at 154—157° (15 mm. ; oil-bath, 175°), and had a rotation $\alpha_D - 24°$, $l = 0{\cdot}4992$, $t = 20°$.

After purification, which, in consequence of the yellow colour, necessitated one more distillation than usual, 6 grams of practically colourless liquid distilling at 157—158° (15 mm. ; oil-bath, 180°) were obtained.

I. 0·1413 gave 0·3290 CO_2 and 0·1343 H_2O. C = 63·50 ; H = 10·56.
II. 0·1373 „ 0·3194 CO_2 „ 0·1290 H_2O. C = 63·44 ; H = 10·44.
Calculated for $C_{13}H_{26}O_4$, C = 63·41 ; H = 10·57 per cent.

$\alpha_D - 24{\cdot}00°$, $l = 0{\cdot}4992$, $t = 20°$, $d\ 20°/4° = 0{\cdot}9527$.
$[\alpha]_D^{20°} - 50{\cdot}46°$; $[M]_D^{20°} - 124{\cdot}13°$.

Dimethoxypropionamide.

Dry ammonia was passed into a solution of ethyl dimethoxypropionate in methyl alcohol kept at 0°. The saturated liquid was then placed in a sealed tube and heated to 120° for six hours. On removing the liquid from the tube, the alcohol and ammonia were allowed to evaporate at the ordinary temperature, and a crystalline residue was left. The latter was recrystallised from methyl alcohol, long, slender needles melting at 77—77·5° being obtained. The same substance was also similarly prepared from propyl dimethoxypropionate. The two preparations were consequently mixed and recrystallised until of constant rotation.

0·1419 gave 13·3 c.c. of moist nitrogen at 734 mm. and 14·5°. N = 10·62.

$C_5H_{11}O_3N$ requires N = 10·53 per cent.

The amide is very soluble in ether, alcohol, and pyridine; it crystallises well from ligroin.

The rotation was determined in methyl alcohol and in pyridine solution respectively.

Rotation of Dimethoxypropionamide.

Methyl Alcohol Solution.

p.	d 20°/4°.	$\alpha^{20°}$. l = 296·2 mm.	$[\alpha]_D^{20°}$.	$[M]_D^{20°}$.
3·1283	0·8012	− 4·05°	− 54·55°	− 72·55°
1·6026	0·7970	− 2·06	− 54·45	− 72·42

Pyridine Solution.

1·6956	0·9788	− 3·52°	− 71·60°	− 95·23°
1·0404	0·9784	− 2·15	− 71·31	− 94·84

Dimethoxypropionic Methylamide.

This was separately prepared from the butyl and the heptyl dimethoxypropionate respectively by passing dry methylamine gas into each of these esters in alcoholic solution. The saturated solutions were further treated in exactly the same way as described above in the preparation of the amide.

The residue left after the removal of alcohol and excess of methylamine was a liquid which only solidified after standing for three weeks in an exsiccator. The solid thus obtained was very deliquescent and was with much difficulty recrystallised from ligroin kept at − 10°; it then exhibited a white, feathery appearance.

The specimens thus obtained from the two different esters gave the same rotation and were, therefore, united and recrystallised.

0·1128 gave 9·7 c.c. moist nitrogen at 741 mm. and 18·5°. N = 9·65.

$C_6H_{13}O_3N$ requires N = 9·52 per cent.

The rotation was determined in methyl alcohol solution.

Rotation of Dimethoxypropionic Methylamide.

Methyl Alcohol Solution.

p.	d 20°/4°.	$\alpha_D^{20°}$. l = 296·2 mm.	$[\alpha]_D^{20°}$.	$[M]_D^{20°}$.
1·8918	0·7962	− 2·62°	− 58·72°	− 86·32°
1·0520	0·7956	− 1·47	− 59·30	− 87·17

Preparation of Calcium Glycerate from Ethyl Dimethoxypropionate.

In order to ascertain whether the configuration of the asymmetric carbon atom had remained unchanged during the transformation

glycerate —> dimethoxypropionate,

calcium glycerate was prepared from some of the ethyl dimethoxypropionate above described.

Ethyl dimethoxypropionate (4·4 grams) was heated with ten times the weight of fuming hydriodic acid in a sealed tube at 100° for 8 hours. The production of an oily layer smelling of methyl iodide showed that the desired action had taken place. The aqueous layer, after most of the hydriodic acid had been driven off by heating *in vacuo*, was extracted with ether and benzene to remove free iodine, and then neutralised with calcium carbonate. After filtering off the excess of calcium carbonate, and concentrating on the water-bath, the calcium glycerate was obtained as a semi-crystalline residue. The latter was dissolved in water, made up to 25 c.c., the rotation determined, and the strength of the solution ascertained by means of a calcium estimation. Thus:

Strength of solution as determined by analysis, $Ca(C_3H_5O_4)_2,2H_2O$.	$\alpha_D^{20^\circ}$ in 198 mm. tube.	
	Recovered calcium glycerate.	Pure calcium glycerate for comparison.
0·8412 gram	−1·20°	−1·03°
0·5216 ,,	−0·75	−0·63

The above concordance between the activity of the original calcium glycerate and that obtained by dimethylation and hydrolysis of the dimethoxypropionic ester shows that the asymmetry of the carbon atom was preserved throughout the whole series of transformations:

Ca-glycerate —> Glyceric ester —> Dimethoxypropionic ester —> Ca-glycerate.

Influence of Temperature on the Rotation of the Dimethoxypropionic Esters.

In the following tables are recorded the determinations of rotatory power for each ester at temperatures between 15° and 100°. In each case, after the rotation had been ascertained at 100°, it was redetermined at 15° in order to see whether the activity had suffered any permanent change through the compound being heated.

1. *Methyl Dimethoxypropionate.*

Temperature.	$\alpha_D^{t°}$. l = 49·92 mm.	Density $t°/4°$.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
15·0°	−37·41°	1·0680	−70·17°	−103·85°
20·0	37·00	1·0634	69·70	103·16
30·5	35·93	1·0484	68·65	101·60
51·5	33·87	1·0304	65·85	97·46
71·0	32·06	1·0110	63·52	94·01
97·3	29·88	0·9827	60·86	90·07
15·0	37·35	—	—	—

Densities determined:

Temperature...	15·4°	20°	30°	60°	80°
Density $t°/4°$...	1·0683	1·0634	1·0489	1·0230	1·0012

2. *Ethyl Dimethoxypropionate.*

Temperature.	$\alpha_D^{t°}$. l = 49·92 mm.	Density $t°/4°$.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
15·0°	−36·45°	1·0340	−70·62°	−114·40°
20·0	36·00	1·0309	69·95	113·32
30·5	34·96	1·0213	68·57	111·08
50·5	33·08	0·9986	66·36	107·50
60·5	32·11	0·9873	65·15	105·54
97·0	29·18	0·9523	61·38	99·44
15·0	36·38	—	—	—

Densities determined:

Temperature...	15·4°	20°	30°	60°	80°
Density $t°/4°$...	1·0344	1·0309	1·0217	0·9878	0·9686

3. *Propyl Dimethoxypropionate.*

Temperature.	$\alpha_D^{t°}$. l = 49·92 mm.	Density $t°/4°$.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
15·0°	−35·23°	1·0138	−69·61°	−122·51°
20·0	34·76	1·0090	69·01	121·46
31·0	33·76	0·9973	67·81	119·35
50·5	31·93	0·9768	65·48	115·24
60·0	31·01	0·9668	64·25	113·08
97·0	27·96	0·9313	60·14	105·85
15·0	35·25	—	—	—

Densities determined:

Temperature..	15·4°	20°	30°	60°	80°
Density $t°/4°$...	1·0141	1·0090	0·9983	0·9668	0·9476

4. n-*Butyl Dimethoxypropionate.*

Temperature.	$\alpha_D^{t°}$. l=49·92 mm.	Density $t°/4°$.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
15·0°	−32·51°	0·9962	−65·37°	−124·20°
20·0	32·13	0·9921	64·88	123·27
33·5	30·85	0·9775	63·22	120·12
57·0	28·86	0·9554	60·51	114·97
97·0	25·85	0·9188	56·36	107·08
15·0	32·35	—	—	—

Densities determined:

Temperature......	15°	20°	30°	60°	80°
Density $t°/4°$......	0·9962	0·9921	0·9813	0·9525	0·9343

5. n-*Heptyl Dimethoxypropionate.*

Temperature.	$\alpha_D^{t°}$. l=49·92 mm.	Density $t°/4°$.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
15·0°	−26·48°	0·9624	−55·12°	−127·88°
20·0	26·20	0·9571	54·84	127·23
35·0	25·08	0·9443	53·20	123·42
54·0	23·68	0·9273	51·15	118·67
96·0	21·11	0·8961	47·19	109·48
15·0	26·39	—	—	—

Densities determined:

Temperature......	15°	20°	30°	60°	80°
Density $t°/4°$......	0·9624	0·9571	0·9487	0·9220	0·9076

6. n-*Octyl Dimethoxypropionate.*

Temperature.	$\alpha_D^{t°}$. l=49·92 mm.	Density $t°/4°$.	$[\alpha]_D^{t°}$.	$[M]_D^{t°}$.
15·0°	−24·35°	0·9552	−51·07°	−125·63°
20·0	24·00	0·9527	50·46	124·13
39·0	22·66	0·9368	48·45	119·19
55·0	21·71	0·9221	47·16	116·01
96·5	19·45	0·8869	43·93	108·07
15·0	24·31	—	—	—

Densities determined:

Temperature......	15°	20°	30°	60°	80°
Density $t°/4°$......	0·9552	0·9527	0·9450	0·9176	0·9008

From the above tables it will be seen that in all cases the rotation diminishes with rise of temperature. Taking the molecular rotation, the diminution between 15° and 97° is as follows:

	Diminution in $[M]_D$ between 15° and 97°.	Percentage diminution in $[M]_D$ per 1° rise in temp.
Methyl dimethoxypropionate	13·8	0·16
Ethyl ,, ,, ...	15·0	0·16
Propyl ,, ,, ...	16·6	0·16
Butyl ,, ,, ...	17·1	0·17
Heptyl ,, ,, ...	18·4	0·18
Octyl ,, ,, ...	17·6	0·17

Thus, whilst there are considerable differences in the absolute amount of the diminution, the percentage diminution is practically the same for all the esters.

It has been previously shown that the glycerates and diacetylglycerates have their rotations increased by rise of temperature (P. Frankland and MacGregor, Trans., 1894, **65**, 769), and the percentage increase in their case is markedly greater than the percentage diminution in the case of the dimethoxypropionates. On the other hand, the actual diminution in rotation in the case of the dimethoxypropionates is greater than the actual increase in rotation in the case of the diacetylglycerates and glycerates.

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XC.—*The Constitution of Barbaloin. Part I.*

By HOOPER ALBERT DICKINSON JOWETT AND CHARLES ETTY POTTER.

BARBALOIN, a crystalline substance obtained from Barbadoes aloes, was first isolated by Smith in 1850 and examined by Stenhouse (*Phil. Mag.*, 1850, [iii], **37**, 481), who assigned to it the formula $C_{17}H_{18}O_7$. With bromine water, it yielded a crystalline tribromo-derivative.

It was further examined by Tilden (Trans., 1872, **25**, 204; 1875, **28**, 1270), who adopted the formula $C_{16}H_{18}O_7$, which was confirmed by Schmidt (*Ber.*, 1875, **8**, 1275). Tilden obtained a crystalline trichloro-derivative, $C_{16}H_{15}O_7Cl_3$, an amorphous acetyl derivative (C = 58·6; H = 5·4 per cent.), and found that, by distillation with zinc dust, barbaloin yielded methylanthracene. When oxidised with nitric acid, oxalic, picric, and chrysammic (tetranitro-? 1 : 6-dihydroxyanthraquinone) acids were formed, whilst with chromic acid aloexanthin, $C_{15}H_{10}O_6$ (? tetrahydroxymethylanthraquinone) (Trans., 1877, **32**, 267), was produced. The latter when distilled with zinc dust yielded methylanthracene. Although Tilden did not propose any

constitutional formula for barbaloin, it would appear that he regarded it as an anthraquinone derivative.

Groenewald (*Arch. Pharm.*, 1890, **228**, 115) next examined barbaloin and proposed the slightly different formula $C_{16}H_{16}O_7$. He obtained two crystalline acetyl compounds, which were regarded as tri- and hexa-acetylbarbaloins respectively; his analytical data, however, are not sufficient to decide between these two derivatives, as the difference in the composition of the various acetyl derivatives is within the limits of experimental error. Groenewald also obtained a well-defined crystalline tribromobarbaloin, from which he did not succeed in preparing a crystalline acetyl derivative, but the amorphous compounds obtained gave results lying between those calculated for a tri- and a tetra-acetyl derivative. He found that barbaloin contained no methoxyl groups. Léger (*Compt. rend.*, 1897, **125**, 185) confirmed the formula $C_{16}H_{16}O_7$, and prepared two amorphous derivatives which he regarded as dibenzoyl- and diacetyl-barbaloins. From the mother liquors resulting from the recrystallisation of barbaloin, he isolated a substance differing slightly in its properties from the latter, which he named *iso*barbaloin.

Tschirch and Pedersen (*Arch. Pharm.*, 1898, **236**, 200) have stated that a trihydroxymethylanthraquinone (aloe-emodin) was produced by the aërial oxidation of barbaloin.

Léger (*Compt. rend.*, 1898, **127**, 234) prepared a crystalline triacetyltrichlorobarbaloin and an amorphous tribenzoyl derivative. He stated that Groenewald's tribromobarbaloin was in reality tribromo*iso*barbaloin, and showed that the behaviour of *iso*barbaloin towards acylating agents was similar to that of barbaloin.

He next (*Compt. rend.*, 1900, **131**, 55) prepared tribromobarbaloin and stated that it differed from the tribromo*iso*barbaloin (Groenewald's tribromobarbaloin) in appearance, solubility, and water of crystallisation. No melting points of the isomerides are given, and the difference in water of crystallisation lies almost within the limits of experimental error, Groenewald having found $4H_2O$, whilst Léger found $3H_2O$, and the latter does not give the experimental details.

Oesterle (*Arch. Pharm.*, 1899, **237**, 81) showed that pure barbaloin, when treated with an alcoholic solution of hydrogen chloride for 24 hours, yielded a trihydroxymethylanthraquinone identical with Tschirch's aloe-emodin and isomeric with the emodin from rhubarb and frangula bark. The aloe-emodin yielded an acetyl compound which Oesterle considered was the diacetyl derivative, but the possibility that it was the triacetyl compound was not excluded. The yield of the emodin from barbaloin was not stated, but no formation of a sugar was observed. He questioned Tilden's conclusions as to the constitution of aloexanthin, but in a later paper (*Arch. Pharm.*, 1903, **241**,

604) he has shown that by the action of chromic acid on aloe-emodin a substance was formed identical with Hesse's rhein, a tetrahydroxymethylanthraquinone isolated from rhubarb. He further showed that aloexanthin was really an impure rhein, and that Tilden's views as to its constitution were correct.

Seel (*Ber.*, 1900, **33**, 3212) gave the results of the oxidation of barbaloin with various reagents, but he was unable to isolate any definite product. With Caro's acid, he obtained tetrahydroxymethylanthraquinone.

Léger (*Compt. rend.*, 1902, **134**, 1111, 1584) stated that by the action of sodium peroxide on barbaloin, formic acid and an aldopentose were formed, in addition to aloe-emodin. He therefore proposed to alter the empirical formula of barbaloin from $C_{16}H_{16}O_7$ to $C_{21}H_{20}O_9$, and suggested the following constitutional formula :—

```
                    OH
      /\-CO-/\
     |  |-CO-|  |
  HO \/        \/ CH3
               O·CH·[CH·OH]3·CHO
                 |
                 CH3
```

Barbaloin was thus regarded by Léger as a new type of glucoside which is not hydrolysed by dilute acids.

The evidence adduced in support of this radical change in the formula of barbaloin is by no means conclusive. No analytical proof is given in support of this change, and the analytical data given in Léger's first paper (*loc. cit.*) agree much better with the old than with the new formula. The most important evidence, namely, the molecular weight of the substance or a closely related derivative, is lacking, but the molecular weight of a crystalline substance formerly described as triacetyltrichlorobarbaloin and now regarded as penta-acetyltetrachlorobarbaloin, is given. Unfortunately, the details of the experiment are not recorded. No detailed evidence is furnished of the identification of the sugar formed, and it is merely stated that a lævorotatory syrup was obtained giving all the reactions of an aldopentose.

In a later paper (*J. Pharm. Chim.*, 1904, [vi], **20**, 145), Léger attempted to obtain further proof of the presence of the sugar, which he has named *aloinose*, and indicated that he obtained a crystalline osazone which, however, does not appear to have been actually isolated or examined.

Aschan (*Arch. Pharm.*, 1903, **241**, 341) made a number of analyses of carefully purified barbaloin, free from *iso*barbaloin, and also some molecular weight determination of barbaloin by the boiling point method, using acetone as the solvent; his results confirm the old formula, either $C_{16}H_{16}O_7$ or $C_{16}H_{18}O_7$.

In view of the conflicting statements made regarding barbaloin, and especially in view of Léger's results, we commenced an inquiry into this subject. As our cooperation in this work has been interrupted, it has seemed desirable to publish the results thus far obtained, and the work will be continued by one of us.

The results of numerous analyses and of two molecular weight determinations of carefully purified barbaloin have confirmed the formula, $C_{16}H_{18}O_7$, first proposed by Tilden, although the analytical results are not very different from those required for Groenewald's formula. As our results agree best on the whole for the formula $C_{16}H_{18}O_7$, we shall for the present adopt it. This formula is also supported by the analysis and molecular weight determination of tribromobarbaloin. Léger's conclusions, with regard to the formula $C_{21}H_{20}O_9$ recently proposed by him and as to the constitution of barbaloin, must therefore be abandoned.

We have carefully repeated Léger's experiments on the formation of aloe-emodin by the action of sodium peroxide on barbaloin, but although the conditions were varied, no aloe-emodin could be isolated. On the other hand, Oesterle's experiments on the action of hydrogen chloride in alcohol on barbaloin and the formation of aloe-emodin were confirmed, but the yield of the latter was very small and this line of inquiry was abandoned.

Our next experiments were made with tribromobarbaloin from which a well-defined, crystalline tetra-acetyl derivative was obtained. Tribromobarbaloin, and probably barbaloin, therefore contains four hydroxyl groups. Both these substances yield methylanthracene by distillation with zinc dust.

Whilst we are unable at this stage of the inquiry to offer any suggestions as to the constitutional formula of barbaloin, we wish to point out that the generally accepted view that it contains an emodin (trihydroxymethylanthraquinone) complex is open to serious objection. If it contains this complex, the formula may be written

$$\{[C_{14}H_4O_2(CH_3)(OH)_3]CH_7O(OH)\},$$

and it is difficult to see how so many hydrogen atoms as are contained in the complex CH_7O can be introduced into any possible formula. On the other hand, the formation of small amounts of emodin and other anthracene derivatives renders it probable that it bears some relation to this parent substance. It is possible that it is not a derivative of methylanthracene, but of a reduced anthracene, thus accounting for the large amount of hydrogen contained in the substance.

Experimental.

Barbaloin was first recrystallised several times from alcohol, but as the melting point (145—150°) of the dried substance was not very sharp, the purified material was again recrystallised from various solvents and the resulting products analysed. The solvents employed were (1) alcohol, (2) ethyl acetate, (3) methyl alcohol, (4) water, and (5) chloroform.

The substance was in each case dried at 105—110° until of constant weight.

(1) 0·0782 gave 0·171 CO_2 and 0·0402 H_2O. C = 59·6 ; H = 5·7.
(2) 0·0976 „ 0·213 CO_2 „ 0·0476 H_2O. C = 59·5 ; H = 5·4.
(3) 0·133 „ 0·2906 CO_2 „ 0·0675 H_2O. C = 59·6 ; H = 5·6.
(4) 0·133 „ 0·290 CO_2 „ 0·0668 H_2O. C = 59·5 ; H = 5·6.
(5) 0·1512 „ 0·3312 CO_2 „ 0·072 H_2O. C = 59·7 ; H = 5·3.
0·855 in 40 phenol gave $\Delta t - 0·51°$. M. W. = 310.
0·394 „ „ $\Delta t - 0·235°$. M. W. = 310.

Of the three formulæ previously proposed

$C_{16}H_{18}O_7$ (Tilden) requires C = 59·6 ; H = 5·6 per cent. M. W. = 322.
$C_{16}H_{16}O_7$ (Groenewald) „ C = 60·0 ; H = 5·0 „ M. W. = 320.
$C_{21}H_{20}O_9$ (Léger) „ C = 60·6 ; H = 4·8 „ M. W. = 416.

These results, in conjunction with those of Aschan (*loc. cit.*), disprove Léger's formula, and, whilst not excluding the formula $C_{16}H_{16}O_7$, point to the correctness of the formula $C_{16}H_{18}O_7$ originally proposed by Tilden. A determination of the specific rotation in 90 per cent. alcohol solution gave the following result :

$$\alpha_D\ -11' ;\ l = 0·5 \text{ dcm.} ;\ c = 4·4 ;\ [\alpha]_D\ -8·3°.$$

Léger found in ethyl acetate solution $[\alpha]_D\ -10·4°$.

Attempts to obtain a well-defined crystalline acetyl derivative with acetic anhydride were unsuccessful, and we were unable to confirm Groenewald's results (*loc. cit.*) with regard to the two substances described as triacetyl- and hexa-acetyl-barbaloins. A satisfactory derivative was, however, obtained by acetylating barbaloin with acetyl chloride and crystallising the crude product from light petroleum. As thus obtained, it formed a light yellow, microcrystalline powder, insoluble in water, but soluble in alcohol; it melted at 95—96°, was apparently identical with Groenewald's triacetylbarbaloin (m. p. 92°), and gave, on analysis, results agreeing with those obtained by Tilden and by Groenewald.

0·1471 gave 0·319 CO_2 and 0·070 H_2O. C = 59·1 ; H = 5·3.
Tetra-acetylbarbaloin, $C_{24}H_{26}O_{11}$, requires C = 58·8 ; H = 5·3 per cent.

Although the analytical results do not enable one to differentiate between the different acetyl derivatives, and we were unable to find a satisfactory method for determining the acetyl groups present, yet the results, taken in conjunction with those obtained with tribromobarbaloin, point to the deduction that the substance examined was a tetra-acetyl derivative. Attempts to prepare crystalline chloroacetyl, benzoyl, and methyl derivatives were unsuccessful. The absence of methoxyl groups was confirmed.

When distilled with zinc dust, a small quantity (0·6 per cent.) of a hydrocarbon was obtained which, after recrystallisation from alcohol, melted at 199—200°.

0·0644 gave 0·2212 CO_2 and 0·0384 H_2O. C = 93·7; H = 6·6.
$C_{15}H_{12}$ requires C = 93·7; H = 6·3 per cent.

The substance was, therefore, methylanthracene.

Sodium peroxide was added to an aqueous solution of barbaloin according to the details given by Léger (*loc. cit.*), and also under varying conditions, but in no case could a substance corresponding to aloe-emodin be isolated. The only evidence of the formation of an anthraquinone derivative was a slight coloration produced by shaking the benzene extract with ammonia.

When barbaloin was treated with hydrogen chloride in alcoholic solution on a water-bath in a reflux apparatus, a very small quantity of a substance having the properties of aloe-emodin was obtained in addition to much unchanged barbaloin. The crystalline substance, after successive crystallisations from glacial acetic acid and toluene, melted at 216—218°, and would thus appear to be identical with the aloe-emodin described by Oesterle (*loc. cit.*). The yield of product was extremely small and all attempts to improve it were unsuccessful.

Tribromobarbaloin, $C_{16}H_{15}O_7Br_3$.

As the experiments with barbaloin did not give very promising results, the tribromo-derivative was prepared and examined. It melted at 191—192° and agreed in all respects with the compound described by Groenewald (*loc. cit.*).

0·0932 gave 0·1165 CO_2 and 0·024 H_2O. C = 34·1; H = 2·9.
0·1732 ,, 0·1744 AgBr. Br = 42·9.
0·318 in 40 phenol gave Δt − 0·11°. M. W. = 535.
$C_{16}H_{15}O_7Br_3$ requires C = 34·3; H = 2·7; Br = 42·9 per cent. M. W. = 559.

Tetra-acetyltribromobarbaloin, $C_{16}H_{11}O_7Br_3(C_2H_3O)_4$, was prepared by boiling barbaloin with five to six times its weight of acetyl chloride in a reflux apparatus for half an hour.

The crude product, obtained by distilling off the acetyl chloride and treating the residue with water, was recrystallised from 70 per cent. alcohol; it formed small, yellow needles melting at 135°, and soluble in alcohol but insoluble in water.

0·1332 gave 0·1906 CO_2 and 0·0368 H_2O. C = 39·0; H = 3·1.
0·211 „ 0·1656 AgBr. Br = 33·4.
0·2044 „ 0·1602 AgBr. Br = 33·3.
$C_{24}H_{23}O_{11}Br_3$ requires C = 39·6; H = 3·1; Br = 33·0 per cent.

The difference in the amount of bromine contained in the several acetyl derivatives which are possible, and the well-defined crystalline character of the compound, enable the composition of this substance to be determined with certainty.

Tribromobarbaloin must therefore contain four hydroxyl groups, and barbaloin in all probability also contains this number.

Attempts to methylate tribromobarbaloin with sodium and methyl iodide were unsuccessful. Treatment with alcoholic hydrogen chloride also gave a negative result, and in both these cases the greater part of the original substance was recovered unchanged. When distilled with zinc dust, methylanthracene (m. p. 199—200°) was obtained.

Numerous experiments have been made with both barbaloin and its tribromo-derivative with various oxidising agents and by fusion with potassium hydroxide, in order to obtain a reasonable amount of definite degradation products, but hitherto without success.

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XCI.—*The Constituents of the Seeds of Hydnocarpus Wightiana and of Hydnocarpus anthelmintica. Isolation of a Homologue of Chaulmoogric Acid.*

By Frederick Belding Power and Marmaduke Barrowcliff.

In a previous paper (Trans., 1904, **85**, 838), one of us, in conjunction with Mr. F. H. Gornall, gave an account of an investigation of chaulmoogra seeds (from *Taraktogenos Kurzii*, King), which afford the chaulmoogra oil of commerce. The fatty oil from the seeds was shown to consist chiefly of the glyceryl esters of members of a homologous series of acids of an entirely new type. The acids of this series have the general formula $C_nH_{2n-4}O_2$, but contain only one ethylenic linking, and therefore must necessarily possess an alicyclic

grouping; they are also characterised by their optical activity. One of these acids was isolated in a pure state, was shown to have the formula $C_{18}H_{32}O_2$, and was designated chaulmoogric acid (compare Power and Gornall, Trans., 1904, **85**, 851).

The fatty oils from the seeds of two species of *Hydnocarpus*, namely, *H. Wightiana* (Blume) and *H. anthelmintica* (Pierre), which belong to the same natural order as *Taraktogenos*, have long been used in Western India and in China respectively for the same medicinal purposes for which chaulmoogra oil is employed.

Hydnocarpus Wightiana (Blume) is the designation of a tree indigenous to the Western Peninsula of India, from South Concan to Travancore. The oil from the seeds has been brought to the notice of Europeans as a substitute for chaulmoogra oil, and has been used in the Bombay Presidency with satisfactory results. The seeds are not an article of commerce.

Hydnocarpus anthelmintica (Pierre) is a tree indigenous to Siam, the seeds of which are exported to China under the name of "Lukrabo," and are known in the latter country as "Ta-fung-tsze" (compare *Pharmacographia Indica*, Vol. I, pp. 146, 148, and *Pharm. J.*, 1900, **64**, 522).

In view of the interesting facts elicited by the investigation of chaulmoogra seeds (*loc. cit.*) and the considerations referred to, it seemed desirable that the seeds of the above-mentioned two species of *Hydnocarpus* should also be chemically examined, more especially with regard to the constituents of their fatty oils, and the present communication embodies the results which have been obtained.

It may be briefly stated that the fatty oils from the seeds of *H. Wightiana* (Blume) and of *H. anthelmintica* (Pierre) very closely resemble chaulmoogra oil both in their physical characters and in their chemical composition. The acids obtained from the respective Hydnocarpus oils consist chiefly of chaulmoogric acid and a lower homologue of the same series, the latter having been isolated from both oils and now also from chaulmoogra oil. This new acid has the formula $C_{16}H_{28}O_2$, and is designated *hydnocarpic acid.*

Hydnocarpic acid crystallises from alcohol in glistening leaflets, melts at 60°, and has $[\alpha]_D + 68°$ in chloroform solution. Like chaulmoogric acid, it contains only one ethylenic linking, and therefore, in consideration of its formula $C_{16}H_{28}O_2(C_nH_{2n-4}O_2)$, must possess an alicyclic grouping.

The seeds of the two species of *Hydnocarpus*, like chaulmoogra seeds, contain smaller amounts of other substances, but these are of minor interest as compared with that attaching to chaulmoogric and hydnocarpic acids, and the record of their identification will be found in the experimental section of the paper.

Experimental.

I. *The Constituents of the Seeds of Hydnocarpus Wightiana (Blume).*

The seeds of *Hydnocarpus Wightiana* not being an article of commerce, a quantity of them was obtained for us in India, and we have further assured ourselves of their genuineness.

Immediately on their arrival, several of the seeds were crushed, brought into contact with water, and the mixture allowed to remain in a corked flask for some hours. As no hydrogen cyanide was developed, it was evident that they contained no cyanogenetic glucoside at the time of their examination by us, although such a substance may have existed in them at an earlier period (compare Power and Gornall, Trans., 1904, **85**, 840).

In order to obtain the fatty oil, the kernels, which represented 75 per cent. of the weight of the seeds, were subjected to powerful hydraulic pressure. This treatment afforded an amount of a fatty oil and of a "press-cake" equivalent, respectively, to 32·4 and 35·4 per cent. of the weight of the entire seeds. By completely extracting the total powdered seed with ether, 41·2 per cent. of oil was obtained.

The Fatty Oil.

The oil from the seeds of *Hydnocarpus Wightiana*, like true chaulmoogra oil (from *Taraktogenos Kurzii*, King), is, at the ordinary temperature, a soft solid, having a faintly yellow colour and a characteristic odour. It gave the following values:

	Expressed oil.	Oil extracted by ether.
Melting point....................	22—23°	22—23°
Specific gravity	0·958 at 25°	0·959 at 25°
$[\alpha]_D$ in chloroform	+57·7°	+56·2°
Acid value	3·8	7·4
Saponification value	207·0	207·0
Iodine value	101·3	102·5

Hydrolysis of the Fatty Oil.

One hundred grams of the oil were hydrolysed with alcoholic potassium hydroxide, the alcohol removed, and the residue mixed with sand, dried, and extracted with light petroleum. The latter yielded a small amount of an oily residue; this was dissolved in warm alcohol, and on cooling the solution a substance separated, which, on recrys-

tallisation from ethyl alcohol, formed glistening needles melting at 132—133°.

0·0266 gave 0·0812 CO_2 and 0·0292 H_2O. C = 83·3 ; H = 12·2.
$C_{26}H_{44}O$ requires C = 83·9 ; H = 11·8 per cent.

The colour reactions of this substance confirmed its identity as phytosterol.

The Fatty Acids.

The potassium salts obtained by the above hydrolysis were dissolved in water, the liquid acidified with sulphuric acid, and the liberated fatty acids taken up by ether. The ethereal solution was then washed, dried, and the ether removed, the last traces of the latter being eliminated by heating the residual oil at 100° for some time. On cooling, a hard, white cake was obtained, representing the total fatty acids. These gave the following values: melting point, 41—44°; $[\alpha]_D$ in chloroform + 60·4°; acid value, 214·0; iodine value, 106·3.

For the investigation of the mixture of fatty acids, 1000 grams of the fat were hydrolysed, the aqueous solution of the potassium salts acidified, and the solid cake of acids collected, washed with water, drained at the pump, and then dried between filter paper. The aqueous filtrate from the fatty acids was distilled in steam, and from the acid distillate a barium salt was prepared. The latter was very small in amount and consisted of the salts of acetic and butyric acids.

The solid mixture of acids was fractionally crystallised from alcohol. The first crystalline crop which separated from the alcoholic solution of the whole of the acids from the 1000 grams of fat weighed 200 grams and melted at 46—48°. On further crystallisation, however, from alcohol and from ethyl acetate, it was obtained in the form of glistening leaflets having the constant melting point of 67—68° and giving the following results on analysis:

0·0792 gave 0·2230 CO_2 and 0·0810 H_2O. C = 76·8; H = 11·4.
0·1030 „ 0·2904 CO_2 „ 0·1056 H_2O. C = 76·9; H = 11·4.
$C_{18}H_{32}O_2$ requires C = 77·1; H = 11·4 per cent.
0·1412 absorbed 0·1270 iodine. I = 90·0.
$C_{18}H_{32}O_2$, with one ethylenic linking, requires I = 90·6 per cent.
1·2032, in alcohol, required NaOH equivalent to 42·7 c.c. of a decinormal solution, which is the calculated amount for $C_{18}H_{32}O_2$.

A solution of 1·8127 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube α_D + 4°15′, whence $[\alpha]_D$ + 58·6°.

It was thus shown that this acid melting at 67—68° was in all respects identical with chaulmoogric acid, first obtained by Power and Gornall (*loc. cit.*) from chaulmoogra oil (from the seeds of *Taraktogenos Kurzii*, King).

The alcoholic mother liquor from the above-mentioned first crystalline crop afforded, by successive concentrations, several further crops of crystals, and then a final mother liquor. The latter, although still containing a considerable amount of substance in solution, deposited nothing further of a crystalline character. The treatment of this mother liquor is subsequently described.

The further crops of crystalline acids were then subjected to a systematic and extended process of fractional crystallisation. All the fractions so obtained were found to melt approximately at 48—50°, but when separating from solution they presented an appearance which, although identical for all the fractions, did not satisfy us that we were dealing with an individual acid. Moreover, evidence of a quantitative nature indicated that the above fractions consisted of a molecular mixture of chaulmoogric acid, $C_{18}H_{32}O_2$, and a homologous acid having the formula $C_{16}H_{28}O_2$. This supposition was subsequently verified, for it has been possible to separate these acids by resorting to a process of fractional precipitation and crystallisation of their barium salts.

Isolation of a Homologue of Chaulmoogric Acid—Hydnocarpic Acid, $C_{16}H_{28}O_2$.

Two hundred and fifty grams of the above fractions melting at 48—50° were dissolved in 1 litre of alcohol. To this solution there was added a solution of 25 grams of barium acetate in the smallest possible quantity of water, the amount of barium acetate thus employed being sufficient to convert one-fifth of the total weight of the fatty acids into barium salts. The fraction of barium salts, which was at once precipitated as a sticky mass, was then dissolved by heating the liquid. On cooling, it again separated, but in a crystalline form; it was collected at the pump and washed with alcohol. The mother liquor from this first fraction of barium salts was then treated with another 25 grams of barium acetate, and a second fraction of barium salts obtained in precisely the same manner as was the first. The whole process was then twice repeated, and the remaining one-fifth of the acids, not being converted into barium salts, was obtained by removing the solvent.

The four fractions of barium salts and the acids from the mother liquor from the fourth fraction of these salts were respectively digested with dilute hydrochloric acid. The regenerated acids were then dissolved in ether, the ethereal solutions washed, dried, the ether removed, and the residues recrystallised from alcohol. The melting points of the several fractions of acids, placed in the order in which the latter were obtained, were as follows: (1) 53—55°; (2) 60—62°; (3)

46—47°; (4) 53—55°; (5) 56—58°. Fraction (2), on recrystallisation from alcohol, gave chaulmoogric acid melting at 67—68°. Fractions (4) and (5) were combined and recrystallised from alcohol. The recrystallised acid then melted at 59—60°, was in the form of lustrous leaflets, and, on further crystallisation from alcohol or ethyl acetate, its melting point remained unchanged.

0·1018 gave 0·2833 CO_2 and 0·1022 H_2O. C = 75·9; H = 11·2.
0·1056 „ 0·2945 CO_2 „ 0·1052 H_2O. C = 76·1; H = 11·1.
$C_{16}H_{28}O_2$ requires C = 76·2; H = 11·1 per cent.

0·3749 required NaOH equivalent to 14·8 c.c. of a decinormal solution, which is the calculated amount for $C_{16}H_{28}O_2$.

0·2608 absorbed 0·2612 iodine. I = 100·2.

$C_{16}H_{28}O_2$, with one ethylenic linking, requires I = 100·7 per cent.

The *silver* salt was prepared and analysed:

0·2724 gave 0·0815 Ag. Ag = 29·9.
0·1700 „ 0·3296 CO_2, 0·1138 H_2O, and 0·0510 Ag.
C = 52·9; H = 7·4; Ag = 30·0.
$C_{16}H_{27}O_2Ag$ requires C = 53·5; H = 7·5; Ag = 30·1 per cent.

It was thus shown that this acid, melting at 59—60°, has the formula $C_{16}H_{28}O_2$, contains only one ethylenic linking, and therefore must possess a closed carbon ring. In other words, it is a lower homologue of chaulmoogric acid, and belongs to the same type as the latter. We have designated this new acid *hydnocarpic acid.*

Hydnocarpic acid, like chaulmoogric acid, is optically active.

A solution of 1·3063 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube α_D + 3°34′, whence $[\alpha]_D$ + 68·1°.

Hydnocarpic acid is only sparingly soluble in the cold in the usual organic solvents, with the exception of chloroform, in which it is easily soluble. An aqueous solution of its sodium salt at once decolorises permanganate in the cold. Like chaulmoogric acid, it remains unattacked by fused potassium hydroxide, even at 250°. The following derivatives of the acid were prepared and characterised.

Methyl Hydnocarpate, $C_{15}H_{27}\cdot CO_2Me$.

Five grams of hydnocarpic acid were dissolved in 25 c.c. of methyl alcohol and 5 grams of sulphuric acid slowly added, when the ester soon separated as an oil. After the mixture had been allowed to stand for some hours, water was added, the oil taken up with ether, the ethereal solution washed with sodium carbonate, then with water, dried, the ether removed, and the ester distilled under diminished pressure.

Methyl hydnocarpate boils at 200—203° (corr.) under 19 mm. pressure, and is a colourless oil, which, however, solidifies when cooled, forming a mass of colourless crystals, melting again at 8°.

0·0973 gave 0·2739 CO_2 and 0·0988 H_2O. C = 76·8 ; H = 11·3.
$C_{17}H_{30}O_2$ requires C = 76·7 ; H = 11·3 per cent.

A solution of 0·9818 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube $\alpha_D + 2°27'$, whence $[\alpha]_D + 62·4°$.

Ethyl Hydnocarpate, $C_{15}H_{27}·CO_2Et$.

This substance was prepared in the same manner as the methyl ester; it boils at 211° (corr.) under 19 mm. pressure, and is a colourless oil.

0·0955 gave 0·2689 CO_2 and 0·0976 H_2O. C = 76·8 ; H = 11·4.
$C_{18}H_{32}O_2$ requires C = 77·1 ; H = 11·4 per cent.

A solution of 0·5087 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube $\alpha_D + 1°3'$, whence $[\alpha]_D + 51·6°$.

Hydnocarpamide, $C_{15}H_{27}·CO·NH_2$.

Five grams of the acid were warmed with a slight excess of phosphorus trichloride. The acid chloride was then dissolved in ether and this solution slowly added to 50 c.c. of concentrated ammonia solution, cooled to 0°. The solid amide, which was at once formed, was collected, washed with water, with dilute sodium hydroxide, again with water, and then recrystallised from ethyl alcohol.

Hydnocarpamide separates from alcohol in clusters of fine, colourless needles which melt at 112—113°.

0·0995 gave 0·2787 CO_2 and 0·1054 H_2O. C = 76·4 ; H = 11·8.
$C_{16}H_{29}ON$ requires C = 76·5 ; H = 11·6 per cent.

A solution of 0·6947 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube $\alpha_D + 1°57'$ at 30°, whence $[\alpha]_D^{30°} + 70·2°$.

The Alcoholic Mother Liquor from Chaulmoogric and Hydnocarpic Acids.

It was stated on p. 888 that after separating from the alcoholic solution of the fatty acids several crystalline crops, which subsequently afforded chaulmoogric and hydnocarpic acids, there remained a final mother liquor which deposited nothing further in a crystalline form, although still containing an appreciable quantity of acids in solution. On the addition of water, these acids separated in an oily

condition. They were dissolved in ether, the ethereal solution washed, dried, and the ether removed. The residual oil, on standing, deposited a small amount of solid acids. The latter were collected at the pump, drained on porous earthenware, and distilled, when the whole passed over at 220—225° under 20 mm. pressure.

0·1327 gave 0·3690 CO_2 and 0·1302 H_2O. C = 75·9 ; H = 10·9.
$C_{18}H_{32}O_2$ requires C = 77·1 ; H = 11·4 per cent.
$C_{16}H_{28}O_2$ „ C = 76·2 ; H = 11·1 „
$C_{14}H_{24}O_2$ „ C = 75·0 ; H = 10·7 „

0·2456 absorbed 0·2638 iodine. I = 107·4.
$C_{18}H_{32}O_2$, with one ethylenic linking, requires I = 90·6 per cent.
$C_{16}H_{28}O_2$, „ „ „ „ „ I = 100·7 „
$C_{14}H_{24}O_2$, „ „ „ „ „ I = 113·4 „

A solution of 0·8902 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube α_D + 2°, whence $[\alpha]_D$ + 56·1°.

The solid fraction, which was obviously a mixture, since it could not be crystallised, would appear to consist of chaulmoogric and hydnocarpic acids, together with a still lower homologue of the same series having the formula $C_{14}H_{24}O_2$.

The filtrate from the above solid fraction amounted to 38 grams. It was distilled under 20 mm. pressure, and the following fractions were collected.

Fraction boiling at 220—225°/20 *mm.*—This was at first wholly an oil, but after a time an amount of solid acids separated.

0·2408 absorbed 0·3109 iodine. I = 129·1 per cent.

Its specific rotatory power in chloroform was $[\alpha]_D$ + 41·9°.

Fraction boiling at 225—230°/20 *mm.*—This was similar to the preceding fraction.

0·3673 absorbed 0·4815 iodine. I = 131·1 per cent.

Its specific rotatory power in chloroform was $[\alpha]_D$ + 46·6°.

Fraction boiling at 230—235°/20 *mm.*—This was the largest of these fractions, and on standing it also partly solidified.

0·1193 gave 0·3401 CO_2 and 0·1212 H_2O. C = 76·6 ; H = 11·0.
0·2330 absorbed 0·3279 iodine. I = 140·7 per cent.

Its specific rotatory power in chloroform was $[\alpha]_D$ + 50·4°.

These three fractions, in view of their high specific rotatory powers, would still appear to contain a large proportion of the members of the chaulmoogric acid series, but their percentage iodine-absorption values, which are appreciably higher than that required for an acid of the

formula $C_{14}H_{24}O_2$ of the latter series, indicate that they also contain an acid or acids belonging to the linolic or linolenic acid series.

There was no evidence of the occurrence of palmitic acid in the fatty oil from *Hydnocarpus Wightiana*, and in this respect it differs from the oil from *Taraktogenos Kurzii*, which contains an appreciable amount of this acid.

Examination of the "Press-cake."

The "press-cake," which remained after the greater part of the fatty oil had been removed from the seeds by expression, was completely extracted with hot alcohol. The greater part of the alcohol was then removed, when a brown, pasty solid was obtained. Two kilograms of the latter were distilled in steam, and the distillate, which contained a small amount of suspended oil, was neutralised with baryta water and extracted with ether. On removing the ether, a limpid, odorous oil was obtained, but which was too small in amount to admit of further examination. The aqueous liquid afforded a very small quantity of a barium salt, which was found to consist of a mixture of barium formate and butyrate. The liquid in the steam-distillation flask consisted of two layers, one being a fatty oil and the other a dark aqueous liquid. On cooling, the fatty oil solidified. The aqueous liquid was separated by means of a linen strainer, and was quite free from any suspended oil.* It was digested with animal charcoal and concentrated to a syrupy consistence, but nothing crystalline separated, even on long standing. It contained a large amount of *i*-glucose, for it readily afforded a phenylglucosazone melting at 216°, and also much proteid matter.

Isolation of a Hydrolytic Enzyme.

A portion of the "press-cake" was digested with water and the filtered liquid mixed with twice its volume of alcohol. After some hours, the precipitate was collected, washed with alcohol, dried over sulphuric acid, and reduced to a powder. The yield of this substance was about 2 per cent. of the weight of the "press-cake." It readily effected the hydrolysis of both amygdalin and potassium myronate.

* In the examination of the "press-cake" from chaulmoogra seeds (Power and Gornall, *loc. cit.*, p. 842), the aqueous liquid which passed through the strainer contained an oil in suspension. It was stated that the latter was hydrolysed with potassium hydroxide, and that, on subsequently extracting with ether, an oil was obtained. The latter was regarded as a substance which could be neither an acid nor an ester. We have since found that, inadvertently, an insufficient amount of potassium hydroxide was employed, and that, therefore, the hydrolysis was not quite complete. The oil which was thus obtained has been ascertained to consist of ethyl esters, formed from the fatty acids during the extraction of the "press-cake" with alcohol.

II. *The Constituents of the Seeds of Hydnocarpus anthelmintica (Pierre).*

A large quantity of these seeds was obtained for us in Siam, and their genuineness verified.

When the kernels from 20 grams of the seeds were crushed and mixed with water, a distinct odour of hydrogen cyanide was soon developed, thus indicating that they contained a cyanogenetic glucoside. An attempt was accordingly made to isolate this substance from 2 kilograms of the seeds, employing the same method as was successful in obtaining gynocardin from the seeds of *Gynocardia odorata*, R.Br. (Power and Lees, Trans., 1905, **87**, 352). The amount of glucoside present was, however, very small, and nothing crystalline was obtained.

The seeds were first divested of their shells, which represented 68·8 per cent. of their weight. The kernels were then subjected to hydraulic pressure, and afforded an amount of a fatty oil and of a "press-cake" equivalent, respectively, to 16·3 and 15 per cent. of the entire seeds. By completely extracting the total powdered seed with ether, 17·6 per cent. of oil was obtained.

The Fatty Oil.

The oil from the seeds of *Hydnocarpus anthelmintica* is, at the ordinary temperature, a nearly colourless, firm solid, having the same characteristic odour as is possessed by both chaulmoogra oil and that from the seeds of *H. Wightiana*. Its values were determined with the following results:

	Expressed oil.	Oil extracted by ether.
Melting point............	24—25°	23—24°
Specific gravity	0·953 at 25°	0·952 at 25°
$[\alpha]_D$ in chloroform	+52·5°	+51°
Acid value	7·5	8·1
Saponification value ...	212·0	208·0
Iodine value	86·4	82·5

Hydrolysis of the Fatty Oil.

One hundred grams of the oil were hydrolysed with alcoholic potassium hydroxide, and the product extracted with light petroleum in the manner described on p. 886. The residue from the petroleum was exceedingly small in amount. After several crystallisations from alcohol, it was obtained in the form of glistening crystals melting at 132—133°, and was identical with the phytosterol obtained from the seeds of *Hydnocarpus Wightiana.*

The Fatty Acids.

From the potassium salts afforded by the above hydrolysis, the mixture of total fatty acids was obtained in the same manner as described on p. 887. It formed a hard, white solid and gave the following values: melting point, 42—43°; $[\alpha]_D$ in chloroform, +53·6°; acid value, 202·5; iodine value, 87·8.

For the identification of the constituents of this mixture of acids 1000 grams of the fat were hydrolysed with alcoholic potassium hydroxide. The aqueous solution of the potassium salts was acidified, the resulting cake of solid acids separated and washed, and the filtrate from the latter distilled in a current of steam. From the acid distillate, a barium salt was prepared, which was very small in amount, and was found to consist of a mixture of barium formate and acetate.

The solid mixture of acids, weighing about 850 grams, was fractionally crystallised from alcohol, just as in the case of the acids from *Hydnocarpus Wightiana*, and a quantity of a pure acid melting at 68° was thus obtained. This proved to be chaulmoogric acid.

0·1168 gave 0·3304 CO_2 and 0·1202 H_2O. C = 77·1; H = 11·5.
$C_{18}H_{32}O_2$ requires C = 77·1; H = 11·4 per cent.

A solution of 1·2014 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube α_D + 2°52′, whence $[\alpha]_D$ + 59·5°.

The alcoholic mother liquor from the chaulmoogric acid afforded a quantity of a substance melting at about 48°, which was apparently identical with the molecular mixture of chaulmoogric and hydnocarpic acids obtained by the crystallisation of the acids from *Hydnocarpus Wightiana* (p. 888). Just as in the latter instance, these two acids were separated by fractionally precipitating and crystallising their barium salts. The hydnocarpic acid thus obtained melted at 59—60°.

0·1330 gave 0·3698 CO_2 and 0·1336 H_2O. C = 75·9; H = 11·2.
0·1224 „ 0·3405 CO_2 „ 0·1230 H_2O. C = 75·9; H = 11·2.
$C_{16}H_{28}O_2$ requires C = 76·2; H = 11·1 per cent.

0·2329 absorbed 0·2336 iodine. I = 100·3.
$C_{16}H_{28}O_2$, with one ethylenic linking, requires I = 100·7 per cent.

A solution of 0·68 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube α_D + 1°51′, whence $[\alpha]_D$ + 68°.

The alcoholic mother liquor from the mixture of chaulmoogric and hydnocarpic acids, which deposited nothing further of a crystalline character, was diluted with water. The resulting oily mixture of acids was dissolved in ether, the ethereal solution washed, dried, and the

ether removed. The residual oil was then distilled under diminished pressure, when it passed over between 214° and 234°/12 mm., and amounted to 40 grams. It was converted into lead salts by dissolving in alcohol and adding a slight excess of lead acetate also dissolved in alcohol. The solution was then evaporated, mixed with sand, the mass dried, and fractionally extracted with dry ether in a Soxhlet apparatus. Two fractions of lead salts soluble in ether were thus obtained. The acids regenerated from the first fraction, on distillation, passed over principally at 221—226°/12 mm. The distilled fraction had the specific rotatory power $[\alpha]_D$ +34·1°, and a percentage iodine-absorption value of 92·4. When treated with mercurous nitrate, it afforded elaidic acid, which proved the presence of oleic acid.

The second fraction of lead salt was crystalline, and was found to consist chiefly of lead hydnocarpate.

The lead salt insoluble in ether and remaining in the Soxhlet apparatus was decomposed, and the regenerated acid, which was solid, crystallised from alcohol. It was finally obtained in needles melting at 60°, was shown to be a saturated acid, and was, in fact, palmitic acid.

0·0953 gave 0·2609 CO_2 and 0·1060 H_2O. C = 74·7 ; H = 12·4.
$C_{16}H_{32}O_2$ requires C = 75·0 ; H = 12·5 per cent.

The "press-cake" was extracted with alcohol, and the alcoholic extract examined in the same manner as that obtained from the seeds of *H. Wightiana.* It afforded a very small amount of acids volatile in steam, which were recognised as formic, acetic, and butyric acids. It also contained much inactive glucose and proteid substances.

The seeds of *H. anthelmintica* afforded, furthermore, 0·3 per cent. of a hydrolytic enzyme, which was isolated in the usual manner; it hydrolyses amygdalin, but does not act on potassium myronate.

Isolation of Hydnocarpic Acid from Chaulmoogra Oil (from Taraktogenos Kurzii, King).

During the investigation of chaulmoogra seeds (Power and Gornall, *loc. cit.*), it was shown that, after the removal of the chaulmoogric acid by crystallisation of the total fatty acids from alcohol, several fractions were obtained, the quantitative examination of which indicated the presence of a lower homologue of chaulmoogric acid. In view of the isolation of hydnocarpic acid from the two sources previously mentioned in this paper, it seemed desirable to attempt to isolate this acid from the fatty oil from *Taraktogenos* seeds.

A quantity of the total fatty acids was therefore fractionally crystallised from alcohol, and a large amount of chaulmoogric acid separated

The mother liquor from the latter acid afforded a large fraction consisting of a pasty solid which could not be crystallised. It was found, however, that by washing with cold alcohol the acids of an oily character were removed, and that the undissolved portion could then be readily crystallised by dissolving in warm alcohol. A large fraction melting at 46—48° was thus obtained, which was apparently identical with the molecular mixture of chaulmoogric and hydnocarpic acids obtained from *Hydnocarpus Wightiana* and *H. anthelmintica.* By fractional precipitation with barium acetate, the two acids were readily separated, and hydnocarpic acid, melting at 59—60°, definitely identified as a constituent of the fatty oil of *Taraktogenos* seeds.

0·1221 gave 0·3405 CO_2 and 0·1222 H_2O. C = 76·1; H = 11·1.
$C_{16}H_{28}O_2$ requires C = 76·2; H = 11·1 per cent.

0·1346 absorbed 0·1338 iodine. I = 99·4.
$C_{16}H_{28}O_2$, with one ethylenic linking, requires I = 100·7 per cent.

A solution of 1·2652 in chloroform, made up to 25 c.c., gave in a 1-dcm. tube α_D +3°26′, whence $[\alpha]_D$ +67·8°.

We desire to express our thanks to Mr. Frederic H. Lees for his assistance in connection with the investigation of these oils.

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XCII.—*The Constituents of the Seeds of Gynocardia Odorata.*

By FREDERICK BELDING POWER and MARMADUKE BARROWCLIFF.

PRIOR to the year 1900 it was generally believed that the "chaulmoogra oil" of commerce was obtained from the seeds of *Gynocardia odorata* (R. Br.). More recently, however, it has been recorded by Mr. E. M. Holmes (*Pharm. J.*, 1900, **64**, 522; 1901, **66**, 596), on the authority of Dr. Prain, Director of the Botanic Survey of India, that chaulmoogra oil is afforded by the seeds of *Taraktogenos Kurzii* (King), these seeds having evidently been wrongly referred to the genus *Gynocardia.* The results obtained by one of us and Mr. F. H. Gornall (Trans., 1904, **85**, 838) in an investigation of the oil from authentic seeds of *Taraktogenos Kurzii* are in accordance with the above observation, for it was proved that the latter oil is identical

in its physical characters and in composition with the chaulmoogra oil of commerce.

We are now, moreover, in a position to state conclusively that the oil which has long been known in European commerce as "chaulmoogra oil," and sometimes described under the synonym of "gynocardia oil," has never been obtained from the seeds of *Gynocardia odorata*, for whereas chaulmoogra oil at the ordinary temperature is a solid (m. p. 22—23°), the oil from the seeds of *Gynocardia odorata* is a liquid. Furthermore, chaulmoogra oil is optically active and consists chiefly of the glyceryl esters of members of the chaulmoogric acid series, whereas the oil from gynocardia seeds is optically inactive and contains neither chaulmoogric acid nor its homologues.

The present investigation has shown that gynocardia oil consists of the glyceryl esters of the following acids: (1) linolic acid, or isomerides of the same series, constituting the largest proportion of the oil; (2) palmitic acid, in considerable amount; (3) linolenic and *iso*linolenic acids, the latter preponderating; and (4) oleic acid, in relatively small amount.

In addition to the fatty oil, gynocardia seeds contain, as has previously been shown (Power and Lees, this vol., p. 349), 5 per cent. of a crystalline glucoside, gynocardin, $C_{13}H_{19}O_9N,1\frac{1}{2}H_2O$, and a hydrolytic enzyme, gynocardase.

Experimental.

The seeds of *Gynocardia odorata* are not collected for commercial purposes, and some difficulty was experienced in obtaining them. Through the kindness, however, of Mr. David Hooper, Curator of the Indian Museum, Calcutta, it has been possible for us to procure a quantity of these seeds sufficient for a complete investigation of their constituents.

According to a private communication from Mr. Hooper, the recognised habitats of *Gynocardia odorata* are Sikkim, Assam, and Chittagong in Bengal, and he also informs us that in Assam the oil is sometimes expressed from the seeds by the natives.

The seeds employed in this investigation were collected in Sylhet, Assam, and their genuineness confirmed by Surgeon-Major Prain, Director of the Botanic Survey of India, by the Reporter on Economic Products to the Government of India, and also by Mr. E. M. Holmes, F.L.S., of London.

On divesting the seeds of their shells it was found that the latter represented 37 per cent. of their weight. The kernels, when subjected to hydraulic pressure, afforded an amount of fatty oil and of a "press-cake" equivalent, respectively, to 19·5 and 40 per cent. of the

weight of the entire seed. By extracting the total powdered seed with ether, 27·2 per cent. of oil was obtained.

The Fatty Oil.

The fatty oil from the seeds of *Gynocardia odorata* is, at the ordinary temperature, a light yellow liquid, having an odour resembling that of linseed oil. It is optically inactive. The expressed oil, and that extracted from the seeds by ether, gave the following values respectively:

	Expressed oil.	Oil extracted by ether.
Specific gravity	0·925 at 25°	0·927 at 25°
Acid value	4·9	5·0
Saponification value......	197·0	199·6
Iodine value	152·8	152·0

Hydrolysis of the Fatty Oil.

One hundred grams of the fatty oil were hydrolysed with alcoholic sodium hydroxide, the alcohol removed, and the residue mixed with sand, dried, and extracted with light petroleum. The latter removed a very small amount of a substance which, after crystallisation from alcohol, melted at 133°, and proved to be phytosterol.

The Fatty Acids.

The sodium salts obtained by the above hydrolysis were dissolved in water, the liquid acidified with sulphuric acid, and the liberated fatty acids taken up by ether. The ethereal solution was then washed, dried, and the ether removed, the last traces of the latter being eliminated by heating the residual oil for some time at 100°. The total mixed fatty acids thus obtained, which partially solidified on standing at the ordinary temperature, gave an acid value of 199·8, and an iodine value of 162·6.

In order to investigate the mixture of fatty acids, 500 grams of the fatty oil were hydrolysed, the acids liberated, and the portion volatile in steam removed. The latter consisted of very small amounts of formic and acetic acids. The non-volatile acids were separated from the aqueous liquid and allowed to stand, when a considerable amount of a crystalline substance was deposited. The latter, which was collected at the pump, amounted to 60 grams; it was dissolved in alcohol and converted into its lithium salt in three successive fractions, each of which, after precipitation, was redissolved by heat, allowed to crystallise, the acid regenerated, and then crystallised from alcohol. The first fraction of acid melted at 60—61°, the second at

59—60°, and the third at 59—61°. On further crystallisation of the first fraction it melted at 62°, and gave on analysis the following figures:

0·1086 gave 0·2991 CO_2 and 0·1220 H_2O. C = 75·1; H = 12·5.
$C_{16}H_{32}O_2$ requires C = 75·0; H = 12·5 per cent.

The solid acid which separated from the total fatty acids was thus shown to be palmitic acid.

The high iodine-absorption value (162·6) of the total fatty acids indicated the presence of linolic acid or acids of the same series, and, taking into consideration the large amount of palmitic acid isolated, also of acids of the linolenic series. For the identification of these acids the method was employed which depends on oxidation with permanganate, and the separation of the corresponding hydroxy-acids (compare Lewkowitsch's *Chemical Technology and Analysis of Oils, Fats, and Waxes*, vol. i, pp. 360—363).

Sixty grams of the oily acids, from which the large amount of palmitic acid had been removed as described above, were therefore oxidised with potassium permanganate, and the following products isolated:

(1) A crystalline acid, melting at 133°.

0·0747 gave 0·1862 CO_2 and 0·0773 H_2O. C = 68·0; H = 11·5.
$C_{18}H_{36}O_4$ requires C = 68·3; H = 11·4 per cent.

This product was thus identified as dihydroxystearic acid, and its formation proved the presence of oleic acid in the fatty oil.

(2) A crystalline mixture, melting at 156—159°.

0·1158 gave 0·2624 CO_2 and 0·1077 H_2O. C = 61·8; H = 10·3.
$C_{18}H_{36}O_6$ requires C = 62·1; H = 10·3 per cent.

This evidently consisted of isomeric tetrahydroxystearic acids, which could not be readily separated. They represented the chief product of the oxidation, and their formation would appear to prove the presence in the fatty oil of isomeric acids of the linolic series.

(3) A crystalline acid melting at 171°.

0·1010 gave 0·2100 CO_2 and 0·0866 H_2O. C = 56·7; H = 9·5.
$C_{18}H_{36}O_8$ requires C = 56·8; H = 9·5 per cent.

This acid was therefore *iso*linusic acid, a hexahydroxystearic acid, and its formation proved the occurrence of *iso*linolenic acid in the fatty oil.

(4) A very small amount of a mixture of acids melting considerably higher than *iso*linusic acid. This, in all probability, contained linusic acid (m. p. 203—205°), the hexahydroxystearic acid derived from

linolenic acid. The presence of the latter acid in the fatty oil was, however, definitely established by the formation of its crystalline hexabromide, which melted at 180—181°.

Our thanks are due to Mr. Frederic H. Lees for his assistance in connection with this investigation.

THE WELLCOME CHEMICAL RESEARCH LABORATORIES,
LONDON, E.C.

XCIII.—*A Contribution to the Study of Alkylated Glucosides.*

By JAMES COLQUHOUN IRVINE, Ph.D., D.Sc., Carnegie Fellow, and ADAM CAMERON, M.A., B.Sc., Carnegie Scholar.

IT has been shown in previous papers (Trans., 1904, **85**, 1049, 1071) that when an alkylated sugar such as tetramethyl glucose is subjected to further alkylation, either by the action of methyl alcohol containing hydrochloric acid or by the joint action of silver oxide and methyl iodide, a mixture of two isomeric pentamethylated glucoses is obtained. In the case of tetramethyl glucose, one of the compounds thus produced is identical with the liquid compound obtained by the methylation of α-methylglucoside, and it is therefore the tetramethyl ether of α-methylglucoside. The other product, which is crystalline and lævorotatory, was considered to be the corresponding derivative of β-methylglucoside.

As the type of stereoisomerism first discovered by Fischer in the alkylglucosides is now known definitely to apply to the pentacyl and other similar derivatives of glucose, it no doubt also exists in the pentamethylated glucoses. Although there seemed therefore no reasonable doubt that the lævorotatory compound to which reference has been made represented the β-isomeride, we considered it advisable to establish this point definitely by preparing the compound by the direct alkylation of β-methylglucoside.

β-Methylglucoside was prepared by Van Ekenstein's method and alkylated directly in the manner previously described for the α-form (*loc. cit.*). The reaction gave a nearly quantitative yield of the same crystalline compound above referred to, and our opinion as to its nature is thus confirmed. As the method of preparation obviates the risk of contamination with traces of the α-isomeride, the specific rotations of the substance in various solvents were redetermined. In

water, alcohol, acetone, and benzene, the values for $[\alpha]_D^{20°}$ were found to be respectively $-17·34°$, $-17·43°$, $-16·56°$, and $-18·07°$.

We also undertook the examination of the conditions under which the α- and β-isomeric alkylated glucosides are converted into each other. The transformation of α- and β-methylglucosides and also of the corresponding penta-acyl compounds has recently been studied by Jungius, Lobry de Bruyn, and others, the reagents used (when the change is carried out in solution) being either alcoholic hydrogen chloride, acetic anhydride containing zinc chloride, or chloroform containing sulphur trioxide. We took advantage of the solubility of our alkylated glucosides in other organic solvents in order to ascertain whether the solvent used plays a specific part in the transformation.

In the first place, we found that prolonged heating at 140° in methyl-alcoholic or benzene solution did not promote the change in question, and heating with sodium methoxide and methyl alcohol was similarly without effect. When small quantities of hydrochloric acid (0·25 per cent.) are dissolved in the solvent, we found that the reversible reaction $\alpha \rightleftarrows \beta$ proceeds at temperatures ranging from 110° to 150° in methyl alcohol, acetone, ether, or benzene, and thus the change takes place independently of the nature of the solvent used. This result seems to exclude Fischer's theory that transformations of this nature depend on the intermediate formation of compounds of an acetal type.

In the case of our solutions in methyl alcohol containing hydrochloric acid, heating was continued at 120° until the rotation became constant, and practically the same equilibrium point was reached in parallel experiments made on the α- and β-forms. Calculating from the constant specific rotation observed, the equilibrium mixture contains 77 per cent. of the α- and 23 per cent. of the β-isomeride. Jungius (*Proc. K. Acad. Wetensch. Amsterdam*, 1903, **6**, 99) found identically the same equilibrium proportions in similar experiments on α- and β-methylglucosides.

In the other solvents used, the change was much slower, and, despite prolonged heating, in no other case was the equilibrium point reached. Thus, whilst a solution of the α-form in methyl alcohol containing 0·25 per cent. of hydrogen chloride attained the equilibrium point mentioned in 30 hours, a similar solution in benzene contained after the same treatment only 16 per cent. of the β-form.

This result seems to us to indicate that moisture plays a part in the change and that the catalytic action of the hydrochloric acid, whatever its nature may be, is probably dependent on the ionisation of the acid. The two experiments were carried out under strictly parallel conditions as to concentration, strength of acid used, temperature, and time of heating. The amount of water present would probably, however, be

greater in the alcoholic solution than in the case of benzene, and this may account for the equilibrium being more readily established in the former solvent.

Our results are therefore in agreement with the idea (E. F. Armstrong, Trans., 1903, **83**, 1310; 1904, **85**, 1044) that the transformation of glucosides takes place without rupture of the γ-oxidic linkage or the temporary addition of the solvent used. We intend to make a more complete study of the mechanism of the interconversion of alkylated glucosides.

We have also succeeded in alkylating β-methylgalactoside, and find that this process gives the same crystalline tetramethyl methylgalactoside (m. p. 38—40°) which we formerly obtained by the methylation of tetramethyl galactose. Our views as to the nature of this substance also are thus confirmed. In this connection we would refer to the experimental part for the description of a compound having the molecular composition and properties of a tetramethyl methylgalactoside, but differing from the well-defined α- and β-isomerides in its very low dextrorotation. The compound in question gave a syrup on hydrolysis which only differed from tetramethyl galactose in its specific rotation, which in alcoholic solution was +3·8° instead of +62·6°.

An explanation of the nature of this compound is offered in the experimental part, along with the data on which the deduction is based.

Experimental.

The β-methylglucoside used in our experiments was prepared by Van Ekenstein's method (*Rec. Trav. chim.*, 1894, **13**, 183—186), a process which depends on the fact that when glucose is condensed with methyl alcohol according to Fischer's original method (*Ber.*, 1893, **26**, 2400), the β-form of the glucoside is first produced, and is afterwards transformed almost completely into the α-variety. By dissolving glucose in methyl alcohol containing 28 per cent. of hydrochloric acid and neutralising the acid as soon as the liquid ceased to reduce Fehling's solution, Van Ekenstein obtained the two isomeric methylglucosides in about equal proportions. The process gives exceedingly good yields of the crystalline glucosides, but the separation of the β-form by fractional crystallisation from alcohol is extremely tedious. We modified the method somewhat by extracting the mixture of the glucosides with a large excess of boiling ethyl acetate. In this way, the α-form was gradually extracted, and the undissolved residue, when examined in alcoholic solution, was found to be practically inactive. The final purification was effected by means of crystallisation from

80 per cent. alcohol, and in this way the pure β-form, showing a specific rotation of $-32\cdot2^\circ$ and melting at 108°, was obtained.

We take this opportunity of expressing our indebtedness to Dr. E. F. Armstrong, who kindly furnished us with an additional quantity of β-methylglucoside and thus enabled us to extend our experiments.

The methylation of the compound was effected as described in previous papers (Trans., 1903, **83**, 1021; 1904, **85**, 1049) by the joint action of silver oxide and methyl iodide, and with a similar result. As the alkylation proceeded, the product became soluble in methyl iodide, and thus the last treatment with silver oxide was carried out in this solvent. It was found to be unnecessary to distil the final product, as, on nucleating with tetramethyl β-methylglucoside from a previous preparation, the liquid solidified completely to a mass of beautiful needles which, after drying on a tile and recrystallisation from alcohol, melted at 40—41°.

0·1340 gave 0·2581 CO_2 and 0·1042 H_2O. C = 52·54; H = 8·84.

$C_{11}H_{22}O_6$ requires C = 52·80; H = 8·80 per cent.

The yield of crystalline product was practically quantitative, and examination of the mother liquors collected during the recrystallisation showed that no trace of the α-isomeride was present. From this we conclude that the direct process of alkylation by means of silver oxide and methyl iodide is not attended by any change in the position of the glucosidic methyl group.

The optical rotatory power of the compound was redetermined, as when produced by the alkylation of tetramethyl glucose the substance is liable to be contaminated with traces of the α-isomeride.

Solvent.	*c*.	*l*.	α^{20°.	$[\alpha]_D^{20^\circ}$.
Water	4·4130	2	−1·53°	−17·34°
Ethyl alcohol	5·0200	2	−1·75	−17·43
Benzene	5·0110	2	−1·66	−16·56
Acetone	5·0080	2	−1·81	−18·07

It will be seen that the rotations here given are greater in the lævorotatory sense than those quoted in a previous paper. In view of the fact that in the present instance the possibility of the presence of the dextrorotatory α-isomeride is excluded, we desire to substitute the above numbers for those already published.

The identity and purity of the alkylated glucoside were confirmed by a study of its hydrolysis. When heated in aqueous solution with 8 per cent. hydrochloric acid, as already described (*loc. cit.*), the rotation was found to increase continuously in the dextrorotatory sense without fluctuation, and practically a quantitative yield of tetramethyl glucose (m. p. 83—84°) was obtained.

We found that the preparation of the alkylated β-glucoside is equally successful if the original material used consists of a mixture of the two isomeric methylglucosides containing not more than 25 per cent. of the α-form. In such cases, however, the alkylated product has to be distilled in a vacuum and the β-form crystallised out from the more volatile fractions.

On hydrolysing a mixture of the two alkylated glucosides obtained in this direct manner, we succeeded in recording a well-defined rise and fall of rotation. The deduction made in previous papers that this phenomenon is significant of the presence of both alkylated glucosides is thus confirmed.

Action of Emulsin on Tetramethyl β-Methylglucoside.

It has already been observed that emulsin effects the hydrolysis of tetramethyl β-methylglucoside, and that during the change the optical activity of the solution alters from lævo- to dextro-rotatory. We endeavoured to follow this reaction quantitatively by means of the polarimeter on the lines laid down by E. F. Armstrong (*loc. cit.*), in the hope of obtaining data by means of which the alkylated glucoside could be correlated with the parent aldose of similar structure. In the first place, one part by weight of the glucoside was dissolved in water (10 parts), finely-powdered emulsin (2 parts) added, and the solution maintained at 39°. At the beginning of the experiment, the lævo-rotation of the solution was higher than the calculated value for the glucoside, and this was found to be due to the fact that the emulsin used (Kahlbaum's) gave a lævorotatory solution when extracted with water at 40°. When a specimen of the enzyme was extracted in this way for 15 days, the water being renewed every third day, all the solutions obtained displayed a feeble, although evident, lævorotation. As Armstrong's method of hydrolysis depends on the nature and not on the magnitude of the optical changes observed, the presence of active materials in the solution does not affect the result. We found, however, that in the foregoing experiment on the β-glucoside the solution very readily became turbid owing to coagulation of the dissolved enzyme. This result seems to be caused either by slight variations in the temperature or by the action of traces of alkali added to promote the multirotation of the hydrolysis product. Filtration was therefore rendered necessary, and this we found to result in a decrease of the lævorotation. Blank experiments made with emulsin and water alone gave similar results. Heating, or addition of a trace of alkali to such a solution, occasioned a turbidity, and after filtration the lævorotation was invariably found to be diminished. We were thus unfortunately unable to apply this method of hydrolysis quantitatively,

but quote the above observations, which indicate that with certain specimens of emulsin changes in rotatory power may be occasioned by the coagulation of the enzyme and thus give rise to misleading results.

Interconversion of the α- and β-Modifications of Tetramethyl Methylglucoside.

Alkylated glucosides, on account of their varied solubility and the well-defined changes in rotatory power which they exhibit on hydrolysis, are well adapted for the study of the mutual interconversion of isomeric glucosides. In our experiments we used the crystalline tetramethyl β-methylglucoside, prepared as already described from β-methylglucoside, and also the liquid α-isomeride similarly obtained from α-methylglucoside.

Both compounds were found to be unaffected in rotation by distillation in a vacuum, and thus no interchange of the glucosidic methyl group takes place in the gaseous state. The α-form was also found to be stable in methyl-alcoholic solution towards the action of sodium methoxide, as solutions containing widely different proportions of the methoxide showed a constant optical activity when preserved for several weeks at 50°.

Methyl alcohol containing 0·25 per cent. of hydrochloric acid is, however, capable of effecting the change, but at moderate temperatures the conversion is extremely slow. Thus a solution of the α-form in this solvent was heated for 60 hours at 40° without exhibiting any appreciable change of rotation, and the conversion into the β-form did not occur. At temperatures ranging from 110° to 150°, however, the reversible reaction $\alpha \rightleftharpoons \beta$ was found to proceed, and positive results were obtained with solutions in alcohol, ether, acetone, or benzene containing small quantities of hydrochloric acid (0·25 per cent.). In carrying out these experiments, duplicate solutions of the pure α- and β-isomerides were prepared, and, after determination of the specific rotation, were heated in sealed tubes for several hours. The conversion into the opposite isomeride was indicated by a rise or fall in the rotation according as the β- or α-form was used as the starting point. That these changes in activity were directly due to interconversion of the glucosides was proved in each case by a careful study of the hydrolysis of the product. During the hydrolysis, the remarkable rise and fall in rotation were observed which we have shown to be characteristic of the mixed glucosides.

The following numbers show the nature and magnitude of the changes in rotation observed owing to transformation of the glucosides.

	Solvent.	Time of heating.	$[\alpha]_D^{20}$. Initial.	$[\alpha]_D^{20°}$. Final.
1. $\beta \longrightarrow \alpha$	Methyl alcohol	50 hours at 120°	−15·0°	+100·8°
2. ,,	Ether............	30 ,, 140	−21·3	+67·0
3. ,,	Benzene.........	30 ,, 140	−19·1	+41·3
4. ,,	Acetone	30 ,, 140	−18·1	+45·1
5. $\alpha \longrightarrow \beta$	Methyl alcohol	30 ,, 120	+142·0	+106·6
6. ,,	Benzene.........	30 ,, 140	+144·7	+120·9

In experiments 1 and 5, the heating was continued for an additional 30 hours in order to ensure the attainment of equilibrium.

In each of the experiments summarised above, the product was isolated by removing the hydrochloric acid by means of barium carbonate and evaporating the filtered solution to dryness. In each case, the residual oil behaved like a glucoside towards Fehling's solution, and thus no hydrolysis had occurred during heating. The product was then dissolved in 8 per cent. hydrochloric acid so as to make a 7 per cent. solution of substance and heated to 80°. At this temperature, the β-form is quickly hydrolysed, whilst the α-form is comparatively stable, and thus the rise in rotation of the solution during the first stages of the hydrolysis is readily determined by polarimetric observations at intervals of 15 minutes.

The following table, which contains the data obtained in experiment I, shows the nature of these changes.

Time.	$[\alpha]_D$.	
0	+100·8°	Rise.
15 minutes at 80°	115·0	Rise.
30 ,, ,, 80	118·8	Rise. / Fall.
60 ,, ,, 100	100·9	Fall.
90 ,, ,, ,, ...	89·5	Fall.
120 ,, ,, ,, ...	87·2	Fall. / Constant.
150 ,, ,, ,, ...	87·0	Constant.

The tetramethyl glucose was isolated in each experiment as already described.

The change $\alpha \rightleftarrows \beta$ was also studied in mixtures of the glucosides, where the proportion of the two forms does not correspond with that of the equilibrium mixture under the conditions of the experiment.

It should be noted that the only solvent in which heating was continued until a constant rotation was observed was methyl alcohol. The end value reached was approximately the same in each case, and corresponded with a mixture of 77 per cent. of the α-form and 23 per cent. of the β-variety.

In other solvents, the change was slower, particularly in the case of benzene, but the interconversion seems to take place independently of the nature of the solvent. The presence of hydrochloric acid in the

solution is, however, necessary. In experiments carried out in pure methyl alcohol or pure benzene, no change in the rotation of either glucoside was observed after heating to 140° for 60 hours, and a mixture of the two glucosides likewise maintained a constant optical activity on similar treatment.

Tetramethyl β-Methylgalactoside.

This compound was prepared similarly to the corresponding glucoside by the direct alkylation of β-methylgalactoside. We have, however, in the first place, to record an abnormal series of results. During previous work we had occasion to prepare a large quantity of α-methylgalactoside by condensing galactose with methyl alcohol at 100° with 0·25 per cent. of hydrochloric acid. The α-form was separated by fractional crystallisation, and a large residue was thus accumulated which presumably contained the β-methylgalactoside. This substance was a clear, yellow, semicrystalline syrup, and it had no action on Fehling's solution until hydrolysed. As it showed only a slight dextrorotation in alcohol or water, we concluded that it consisted mainly of the feebly dextrorotatory β-methylgalactoside, and we therefore utilised the material for the preparation of tetramethyl-β-methylgalactoside by alkylation. The alkylation apparently proceeded normally, and the product was therefore distilled under reduced pressure (140—142°/14 mm.). Analysis showed the substance to have the composition of a fully methylated galactoside, and the molecular weight in benzene by the cryoscopic method was normal. Hydrolysis of this compound with 8 per cent. hydrochloric acid at 100° gave a syrup, which distilled under reduced pressure without decomposition and reduced Fehling's solution actively. In composition and otherwise, the substance resembled tetramethyl galactose. Thus, when heated with silver oxide and methyl iodide, it gave a glucosidic product which analysis showed to be a tetramethyl methylgalactoside.

In other respects, however, the results were quite abnormal. The specific rotation in alcohol of the liquid tetramethyl methylgalactoside, obtained in the foregoing manner by alkylating the supposed mixture of α- and β-galactosides, was +4·6°, a number which accorded with our expectations that it contained a large proportion of tetramethyl β methylgalactoside; the liquid, however, despite repeated fractionation, could not be made to crystallise when nucleated with crystals of this compound, and, although on hydrolysis a rise and final fall of rotation were detected, these changes, contrary to expectation, were only slight. Further, the methylated sugar obtained from this hydrolysis displayed a very low rotatory power in alcohol ($[\alpha]_D$ +3·8°), whilst that of tetramethyl galactose is +62·6°, and the

glucosidic product obtained from it by remethylation was practically inactive.

The following table contains a comparison of the composition and properties of the compound under consideration with liquid tetramethyl α-methylgalactoside:

Tetramethyl α-Methylgalactoside.	*Isomeric Compound.*
Colourless liquid of a glucosidic nature.	Colourless liquid behaving like a glucoside.
Composition (calculated): C = 52·80; H = 8·80; CH_3O = 62·0 per cent.	Composition (found): C = 52·71; H = 8·76; CH_3O = 61·85 per cent.
Molecular weight (calculated) = 250.	Molecular weight (found) = 243.
Boiling point: 136—137° under 11 mm. pressure.	Boiling point: 140—142° under 14 mm. pressure.
$[\alpha]_D^{20°}$ in alcohol + 109·9°.	$[\alpha]_D^{20°}$ in alcohol + 4·6°.
Hydrolysed with a great decrease in rotatory power to give a reducing sugar.	Also hydrolysed to a reducing sugar. Rotation decreased very slightly.
Composition of tetramethyl galactose: C = 50·85; H = 8·47; CH_3O = 52·54 per cent.	Composition of the reducing sugar formed: C = 50·37; H = 8·42; CH_3O = 51·6 per cent.
Boiling point of sugar: 172° under 13 mm. pressure.	Boiling point of sugar: 170—172° under 12 mm. pressure.
$[\alpha]_D^{20°}$ in alcohol + 62·6°.	$[\alpha]_D^{20°}$ in alcohol + 3·8°.
Tetramethyl galactose reacts with methyl iodide and silver oxide to give the mixed galactosides boiling at 135—140° under 11 mm. pressure and containing CH_3O = 62·0 per cent.	Also reacted with methyl iodide and silver oxide to give a glucosidic liquid, boiling point 135—140° under 13 mm. pressure. CH_3O = 63·2 per cent.

It will be seen that a complete parallel is established between the syrupy galactoside used and α-methylgalactoside save that the compounds given by the former on alkylation and hydrolysis are almost inactive. From the fact that the molecular composition and reactive powers are identical in each case, it may be deduced that the compounds of low rotation are either partially racemised or have a different configuration from galactose. The latter view is unlikely, as in general the introduction of a methyl group into the glucosidic position or the reverse change of the hydrolysis of a glucoside is attended by a marked change in rotatory power. It will be seen that in the present case hydrolysis only effected a small decrease in the specific rotation and therefore presumably only a small proportion of active material was present. Our results appear to favour the view that the compounds examined were essentially racemic forms, although this idea assumes that racemisation had taken place in all four asymmetric systems contained in the galactose molecule.

In this connection, it should be noted that in his condensation of

galactose with methyl alcohol (*Ber.*, 1895, **28**, 1154) Fischer states that in addition to the two isomeric methylgalactosides, a third substance of a glucosidic nature is produced. This compound was evidently formed by the long-continued action of methyl alcohol containing 0·25 per cent. of hydrochloric acid on either galactoside, and it seems likely that the alkylated products described above represent the methylated derivatives of this unknown substance.

The above results emphasise the importance of starting with glucosides of known composition and purity in work on alkylated sugars, as otherwise the values obtained for the specific rotations may be incorrect.

For the preparation of pure crystalline β-methylgalactoside we adopted the process which Van Ekenstein describes for the corresponding glucoside. The same difficulty was experienced in separating the α- and β-forms, but slow crystallisation from 80 per cent. alcohol gave the desired compound melting at 106—109° and showing practically no rotation in alcoholic solution.

Alkylation gave a nearly quantitative yield of a glucosidic oil which crystallised readily when nucleated with tetramethyl β-methylgalactoside. After drying on a tile and recrystallisation from light petroleum, the crystals melted at 38—40°.

C = 52·62 ; H = 8·80.

$C_{11}H_{22}O_6$ requires C = 52·80 ; H = 8·80 per cent.

The specific rotations of the compound were redetermined.

Solvent.	*c.*	*l.*	$\alpha^{20°}$.	$[\alpha]_D^{20°}$.
Ethyl alcohol	2·720	2	− 1·14°	− 20·98°
Water	2·082	2	+ 1·30	+ 31·22

The numbers already published by us, − 20·9° and + 30·7° respectively, are thus confirmed and the preparation correlates our crystalline alkylated methylgalactoside with β-methylgalactoside.

In conclusion, we desire to express our thanks to Professor Purdie, who placed his research laboratory at our disposal and gave us the benefit of his kindly interest and advice, and also to the Executive Committee of the Carnegie Trust for defraying the entire cost of the investigation.

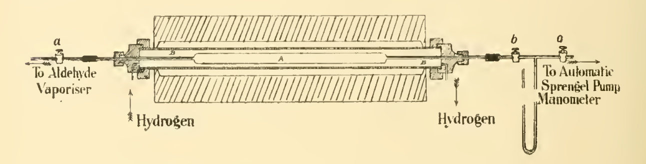
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XCIV.—*The Thermal Decomposition of Formaldehyde and Acetaldehyde.*

By WILLIAM ARTHUR BONE and HENRY LLEWELLYN SMITH.

A KNOWLEDGE of the behaviour of formaldehyde and acetaldehyde at high temperatures is essential to the correct interpretation of the reactions concerned in hydrocarbon flames, and we have accordingly made a number of experiments at temperatures between 400° and 1150°, the results of which are summarised in this paper.

The general arrangement of the apparatus employed in most of the experiments is shown in the accompanying diagram. The vapour of



the aldehyde under investigation was admitted into the vacuous glazed porcelain tube, A (28·5 cm. long, 1·3 cm. internal diameter, capacity = 34 c.c.), which had been previously heated to the desired experimental temperature. The body of A terminated in long narrow ends (2 mm. bore) which projected for some distance beyond the heated zone. The cold ends were joined by stout pressure tubing to the glass stopcocks, *a* and *b*, through which connection could be made with the aldehyde vaporiser or with the manometer, M, and thence, through the stopcock, *c*, with an automatic Sprengel pump, as circumstances required.

A small glass worm (not shown in the diagram) containing about 5 c.c. of water was inserted between the stopcock *c* and the pump.

To ensure the uniform heating of A it was fixed, by means of brass joints with stuffing boxes, co-axially with the wider porcelain tube, B (45 cm. long and 1·7 cm. internal diameter); the two tubes rested on the bed of a powerful furnace (35 cm. long), the gas supply of which was regulated by a Stott governor. A slow current of dry hydrogen was maintained through the annular space between A and B, during the whole of each experiment. All temperatures were determined by means of a Le Chatelier thermo-junction.

Before the aldehyde vapour was admitted to the vacuous tube, the stopcocks *a* and *c* were closed, whilst *b* remained open, thus leaving the tube in connection with the manometer only. Immediately after

the admission of the vapour, *a* was again shut, and the movement of the mercury in the manometer observed during the whole period of heating. At the end of each experiment, the gases in *A* were withdrawn by the pump, through the water in the glass worm, into tubes over mercury, where they were allowed to remain in contact with sticks of zinc chloride for several hours (to ensure the removal of traces of aldehyde vapour) before being analysed. After the tube *A* had been completely exhausted, it was finally burnt out with oxygen in order to prove whether or not the decomposition of the aldehyde had been attended by any separation of carbon.

A. *Experiments with Formaldehyde.*

(*a*) Experiments with formaldehyde vapour were made at 400°, 500°, 700°, 900°, and 1125°. At all temperatures above 700°, practically the whole of the vapour decomposed into carbon monoxide and hydrogen as soon as it entered the hot tube; the manometer never, in fact, indicated any rise in pressure after the tube had once been filled at atmospheric pressure, an operation which did not occupy more than two or three seconds. At 500°, a slight increase in pressure was observed when the tube was very quickly filled, but not if the admission of the vapour extended over 15 or 20 seconds. In the experiments at 400°, the manometer indicated an increase in pressure of about 100 mm. within the first minute after the tube had been filled at the atmospheric pressure; any further increase in pressure was always very small.

Although the decomposition above 500° was so extremely rapid, it never seemed to be quite complete; traces of formaldehyde could usually be detected in the exit gases even at 1125°. These observations cannot, however, be accepted as absolute proof that the decomposition is reversible, since traces of vapour might have been shot through the tube during the filling operation, and have condensed in the cold capillary connections leading to the manometer. Whilst the gaseous products were mainly composed of nearly equal proportions of carbon monoxide and hydrogen, they always contained a small quantity of a saturated hydrocarbon, presumably methane, as well as traces of carbon dioxide. There can be no doubt, however, that at all temperatures decomposition mainly occurs in accordance with the equation $H_2{:}C{:}O = H_2 + CO$.

In the experiments at 400° and 500°, however, there were indications that the main decomposition was accompanied by some more complex change involving a preliminary "condensation" of a portion of the vapour. Thus, for instance, after the tube had been filled at 400°, the manometer indicated a momentary diminution followed by a rapid increase in pressure.

It is important to observe that in none of the experiments was there the slightest separation of carbon. The significance of this fact in connection with the subject of hydrocarbon combustion will be considered in a future communication.

The details of a typical series of experiments are tabulated below:

Temperature.		400°.	500°.	700°.	900°.	1125°.	1125°.
Duration of heating.		2 minutes.	2 minutes.	2 minutes.	2 minutes.	1 minute.	1 minute.
Percentage composition of products.	CO_2	trace	0·25	0·40	0·5	0·4	0·4
	CO	52·7	50·75	50·20	49·4	49 8	49·6
	H_2	45 2	47·00	48·75	49·1	48·9	49·0
	CH_4	2·1	2·00	0·65	1·0	0·9	1·0

(*b*) The question whether or not the decomposition of formaldehyde is to any appreciable extent reversible under the conditions just described is of interest in connection with the subject of flame reactions.* It has been shown in a previous paper (Bone and Wheeler, Trans., 1903, **83**, 1087) that no detectable quantity of formaldehyde is produced when a mixture of equal volumes of moist carbon monoxide and hydrogen is continuously circulated over a hot surface of porous porcelain for two days at 460—480°. We have twice repeated this experiment with the same negative result.

In two other experiments we have circulated a similar mixture, saturated with moisture at 14° and 26° respectively, in an apparatus comprising (1) the porcelain tubes A and B heated to a temperature of from 1050—1080°, (2) a cooled worm containing about 20 c.c. of water, (3) a manometer and automatic pump with the necessary return connections. The total capacity of the apparatus was about 250 c.c. Each experiment lasted 4 hours, and the gaseous mixture (pressure = 438 and 400 mm. respectively) completed a circuit once every 10—15 minutes. The results were, however, entirely negative; there was little or no alteration in pressure (if anything a slight increase, but certainly under 1 per cent.) and no detectable formation of formaldehyde. The Schiff's reagent used for the tests was very sensitive, and gave a distinct reaction with a solution containing one part in a million of formaldehyde.

It was our original intention to pursue the inquiry further in this

* We may take this opportunity of stating that one of us, in conjunction with Dr. Julien Drugman, has detected the formation of aldehydes in hydrocarbon flames, and that for a long time past we have been working on the subject.

direction, as part of the investigation on hydrocarbon combustion on which one of us is engaged. On finding, however, that Messrs. D. L. Chapman and A. Holt had started experiments on the conditions of the formation of formaldehyde (if any) in the system CO_2, CO, H_2 and H_2O at high temperatures, we decided to leave the further working out of the matter in their hands.

(*c*) The changes which occur when the vapour of formaldehyde is kept at 350° in borosilicate glass bulbs under considerable pressure, or is slowly passed, undiluted, over a hot surface of porous porcelain, cannot be represented by any simple equation. The effect of pressure, in absence of oxygen, on the undiluted vapour is to promote a series of "condensations" or polymerisations, and the resultant molecular complexes subsequently break up again yielding simple gaseous products. In the experiments with borosilicate glass bulbs there was no separation of carbon, but oily intermediate products were formed. The gases consisted mainly of carbon monoxide and hydrogen, but the ratio CO/H_2 was high and variable. In one experiment in which the undiluted vapour was passed over porous porcelain at 475° the gaseous products contained :

$CO_2 = 19{\cdot}35$; $CO = 44{\cdot}90$; $H_2 = 24{\cdot}7$; saturated hydrocarbon = 11·05 per cent.*

Some water was formed, and there was also a little darkening of the white surface of the porcelain.

Such complex changes as are here indicated do not, we believe, come into play to any appreciable extent in combustion processes, where the formaldehyde has only a very brief existence ; it either very rapidly falls a victim to the oxygen, or decomposes simply into carbon monoxide and hydrogen.

B. *Experiments with Acetaldehyde.*

(*a*) *At* 400°.

At this temperature, much of the aldehyde decomposed as soon as it entered the hot tube ; the following pressure records, however, indicate the rather slow disappearance of last portions of the vapour.

	Pressure after						
	0.	1.	2.	5.	10.	60	minutes.
Expt. I.	756	860	868	—	—	—	mm.
„ II.	794	940	—	—	972	—	„
„ III.	755	892	—	990	—	1048	„

* The ratio *C/A* obtained in the explosion of the residual gas after removal of oxides of carbon and hydrogen was 1·53.

There was no carbon deposited in any of these experiments, the gaseous products consisting of practically equal volumes of methane and carbon monoxide, as is shown by the following typical analysis:

$$CO_2 = 0{\cdot}3\ ;\ CO = 50{\cdot}2\ ;\ CH_4 = 49{\cdot}5 \text{ per cent.}$$

The ratio C/A obtained in the explosion analysis of the residual gas after removal of the oxides of carbon was exactly 2·00, proving the absence of hydrogen. The decomposition at this temperature may therefore be expressed by the equation:

$$CH_3{\cdot}CHO = CH_4 + CO.$$

(*b*) *At* 600°.

At this temperature, a very rapid decomposition took place, although the last traces of aldehyde again disappeared rather slowly. The following are the pressure records of two typical experiments which extended over 2 and 10 minutes respectively.

	Pressure in mm. after			
	0.	1.	2.	10 minutes.
Expt. I.	773	803	807	—
,, II.	781	810	—	838

In each experiment, some carbon was deposited in the hot tube, and the gaseous product contained hydrogen, as well as methane and carbon monoxide, but no acetylene. Their percentage composition was as follows:

	Expt. 1.	Expt. 2.
Carbon monoxide	48·7	48·0
Methane	45·7	43·0
Hydrogen	5·6	9·0

An interesting point about these results is the appearance of carbon and hydrogen in the products. Now methane itself, we have found, does not decompose into carbon and hydrogen below 800°, and even then very slowly. When, however, we consider that the decomposition of acetaldehyde into methane and carbon monoxide involves the dissolution of the bond between the two carbon atoms and the wandering of a hydrogen atom from the sphere of attraction of the one carbon into that of the other, the partial breaking down of the system at 600° into carbon, hydrogen, and carbon monoxide is not difficult to understand.

(c) *At* 800°.

At this temperature, there was a still greater formation of carbon and hydrogen at the expense of methane, and also traces of acetylene could be detected in the products. We need only give the percentage composition of the gases obtained in two experiments, which extended over 2 and 10 minutes respectively.

	Duration of heating.	
	2.	10 minutes.
Carbon dioxide and acetylene ...	0·5	0·75
Carbon monoxide	42·3	40·10
Methane..............................	26·3	20·75
Hydrogen	30·9	38·40

(d) *In Borosilicate Glass Bulbs at* 350°.

Experiments were also made in which borosilicate glass bulbs filled with the aldehyde vapour at 30° and under atmospheric pressure were maintained at 350° for 24 hours. The products of decomposition, which were under considerable pressure, consisted of practically equal proportions of carbon monoxide and methane; there was neither separation of carbon nor liberation of hydrogen.

(e) *At* 450—500° *in Contact with Porous Porcelain.*

The changes which occur when the undiluted vapour of acetaldehyde is slowly passed over a hot surface of porous porcelain are materially different from those already considered. For these experiments, the apparatus was so arranged that the aldehyde vapour traversed a Jena glass combustion tube (80 cm. long) closely packed with porous porcelain heated to 450—500°. The volatile products of decomposition passed onwards into a large empty worm, where liquids condensed, and from thence through a wash bottle containing water. The gaseous products were afterwards collected over mercury, and, after remaining in contact with sticks of zinc chloride for several days, were finally analysed. The aldehyde very rapidly decomposed; pungent, white fumes issued from the combustion tube and condensed in the dry worm, whilst much gas was obtained, and the white porcelain surface was blackened with a deposit of carbon.

The condensable liquid products separated into an aqueous portion and a brown, pungent oil, which mainly consisted of unsaturated aldehydes (crotonaldehyde, &c.). The gases obtained in one experiment consisted of ethane and carbon monoxide in nearly equal proportions, whilst those from another experiment contained

$CO_2 = 2{\cdot}5$; $CO = 50{\cdot}0$; $CH_4 = 18{\cdot}7$; $C_2H_6 = 13{\cdot}8$, and C_2H_4, &c., = 14·0 per cent.

Evidently, therefore, the porcelain had induced the aldol condensation, which would, of course, give rise to crotonaldehyde and steam. The production of ethane, carbon monoxide, and carbon may be referred to a dimolecular condensation, thus :

$$\begin{array}{l} CH_3\cdot C{<}^{O}_{H} \\ CH_3\cdot C{<}^{O}_{H} \end{array} = \begin{array}{c|c|l} CH_3 & CO & \\ | & - & HOH. \\ CH_3 & C & \end{array}$$

Such complex changes can, however, hardly play any very prominent part in combustion phenomena when the aldehyde is always much diluted and very rapidly burnt by oxygen, and we have not, therefore, made any very detailed study of them.

In conclusion, we have pleasure in thanking Mr. G. W. Andrew, B.Sc., for some valuable help during the later experiments, and also the Government Grant Committee of the Royal Society for grants which have partly defrayed the expenses connected with the work.

THE UNIVERSITY,
MANCHESTER.

XCV.—*The Synthesis of Formaldehyde.*

By DAVID LEONARD CHAPMAN and ALFRED HOLT, jun.

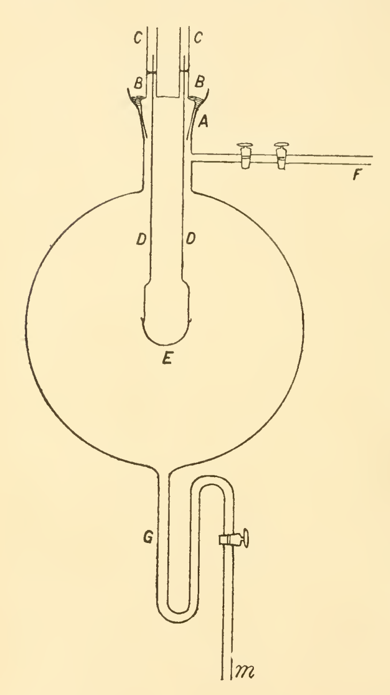
THE conditions determining the formation of formaldehyde from simple gases are interesting from more than one point of view. For example, if it could be shown to be one of the substances occurring in the "producer" or in the "water-gas" system, its presence could not be overlooked in the consideration of the simplest examples of combustion. Formaldehyde, again, in its bearing on the question of the assimilation of carbon by plants is of no less interest. In this connection, O. Loew (*Ber.*, 1888, **21**, 270) has shown that in specified circumstances sugars result from the condensation of formaldehyde, and J. N. Collie (Trans., 1901, **79**, 1063) has put forward several probable suggestions with reference to the nature of the changes involved.* Brodie (*Proc. Roy. Soc.*, 1873, **22**, 172) proved that formaldehyde is produced when the silent discharge is passed through a mixture of carbon dioxide and hydrogen. He had previously observed (*Proc. Roy. Soc.*, 1872, **21**, 245)

* References to work dealing with the possible existence of formaldehyde in plants can be obtained from *The Synthesis of Vital Products*, by R. Meldola.

that marsh gas is obtained under the same conditions from carbon monoxide and hydrogen. Losanitsch and Jovitschitsch (*Ber.*, 1897, **30**, 136), De Hemptinne (*Bull. Acad. Roy. Belg.*, 1897, **34**, 269), and Solvay and Slosse (*Bull. Acad. Roy. Belg.*, 1898, **35**, 547), who repeated the last-mentioned experiment of Brodie, have found formaldehyde in the products. The evidence that formaldehyde is produced both when a mixture of carbon dioxide and hydrogen and also when one of carbon monoxide and hydrogen are submitted to the influence of the silent electric discharge is accordingly conclusive. The work referring to its production without employing the agency of the silent discharge is not so comprehensive. Sixteen years ago it was stated by Jahn (*Ber.*, 1889, **22**, 989), in a short preliminary notice, that carbon monoxide united with the hydrogen absorbed in spongy palladium with the formation of formaldehyde. The work has, so far as we know, neither been confirmed nor extended. Bach (*Compt. rend.*, 1898, **126**, 479) has shown that carbon dioxide in aqueous solution is reduced to formaldehyde by the hydrogen absorbed in palladium, but does not mention whether a similar change takes place when the reacting substances are in the gaseous condition.

Some of our experiments with a mixture of carbon monoxide and hydrogen furnished results of an almost negative character. Of these—as the cause of the small yield of aldehyde is as yet a matter of uncertainty—a short account will suffice. The experiments in question deal with the interaction of carbon monoxide and hydrogen at a low temperature in the presence of a nickel surface. We were influenced in our choice of nickel as a catalysing surface by reason of its energetic action on carbon monoxide, a property which at least points to the possibility of its being the best means of accelerating the reaction between the two gases. The nickel in the form of closely wrapped gauze was contained in a hard glass tube which, during the experiment, was maintained at a temperature of 480—500°. A slow stream of the gases mixed in different proportions was passed backwards and forwards through the tube for periods of time varying in the different experiments from 3 to 8 hours. The products after passing over the heated nickel gauze were led first through ice-cold water and then through a dilute solution of baryta in order to remove the aldehyde and carbon dioxide. The gases were sometimes used in the dried and at other times in the moist condition. As was to be expected, carbon was formed in the presence of the nickel, and the baryta water was almost instantly rendered turbid by the liberated carbon dioxide. The gas issuing from the heated portion of the tube deposited moisture on cooling, and the water contained in solution some organic substance which was not identified. After an experiment, the ice-cold water was first boiled for a short time to expel

carbon monoxide, and then tested for aldehyde. In no case could distinct evidence of an aldehyde be obtained with Schiff's reagent, although the presence of a minute quantity of formaldehyde was indicated by the delicate test recently published by W. B. Ramsden (*Mem. Manchester Phil. Soc.*, 1905, **33**, 49). In one case, an experiment was tried under similar conditions to those described above, but with porous porcelain (containing finely divided platinum within its interstices) as a catalyser. No formaldehyde could, however, be discovered with Schiff's reagent in the products obtained (Bone and Wheeler, Trans., 1903, **83**, 1087). In spite of the fact that Jahn, under conditions not very different from those employed by us, obtained formaldehyde in sufficient quantity to impart its characteristic smell to the water in which it was collected, frequent failure on our part to obtain more than the slightest indication of this substance induced us to alter the method of procedure. The gases were heated with a wire raised to incandescence by an electric current instead of being passed through a hot tube. We have succeeded in showing that when hydrogen is heated with carbon dioxide, and when carbon monoxide (alone or mixed with hydrogen) is heated with steam by means of platinum wire, formaldehyde is produced in appreciable quantity.



The gases were contained in a large glass globe (Fig. 1) with a ground glass joint, *A*, at the neck. Attached to the glass joint were two tubes, *B* and *B'*, into which the thick platinum wires, *D*, *D'*, were fused. Above the protruding ends of the platinum wires, two tubes, *C*, *C'*, served as mercury cups. The fine platinum wire, *E*, was sus-

pended from hooks at the end of *D* and *D′*, and could therefore be easily replaced in the event of its fusing. The gases were admitted to the globe by means of the tube, *F*. The bottom of the globe communicated with a U-tube, *G*, which was kept cool during an experiment. To the end *m* of the U-tube a manometer was attached.

The hydrogen was prepared by the electrolysis of dilute sulphuric acid. The carbon monoxide was obtained either from sodium formate or formic acid by the action of sulphuric acid, according to the directions given by Prof. Dixon (*Phil. Trans.*, 1893, **184**, 167), and was washed by passing it through a solution of caustic alkali. The gases were collected in glass gas-holders over water.

Some precautions must be observed in applying Schiff's test. We find that the reagent is most easily prepared by saturating a strong solution of rosaniline hydrochloride with sulphur dioxide, and then removing the excess of sulphur dioxide with the water-pump. Bone and Drugman add a few drops of the reagent to the liquid to be tested, and then, after several hours, acidify with hydrochloric acid, whereby the difference between the test and the blank is intensified. We find that by substituting sulphuric for hydrochloric acid the tint assumed by the aldehyde solution is blue instead of violet, so that there is a still greater contrast. If the test is performed in this way, the colour obtained with acetaldehyde is quite distinct from that given by formaldehyde, the former on standing becoming green and the latter blue.

An experiment was performed in the following way. The globe was first exhausted and then the gases were separately admitted by means of a three-way tap attached to the tube *F*, the amount of each gas introduced being indicated by the manometer. The U-tube, *G*, was surrounded by cold water during the experiment. The fine platinum wire was heated electrically, and maintained at a temperature near the melting point of platinum.

Experiments with Carbon Monoxide and Hydrogen.

I. Volume of $CO = 330$. Volume of $H_2 = 335$.

The heating was continued for 18 hours with the wire almost at a white heat. The contraction, on cooling, was found to be 9/665ths of the total volume. The liquid in the U-tube gave a faint but distinct aldehyde reaction with Schiff's reagent.

II. Volume of $CO = 288$. Volume of $H_2 = 262$.

The wire was heated to bright redness for 3 hours, and to whiteness for another hour. The final pressure was not taken owing to the breaking of the globe. The water in the globe gave a very faint aldehyde reaction with Schiff's reagent.

The two experiments prove that aldehyde is formed with difficulty when equal volumes of carbon monoxide and hydrogen, saturated with water vapour at the ordinary temperature, are heated together under the conditions of the experiment.

Experiments with Carbon Dioxide and Hydrogen.

I. Volume of $CO = 273$. Volume of $H_2 = 331$.

The wire was heated almost to whiteness for a little over 5 hours. The contraction, on cooling, was found to be 219 volumes, which is 80·2 per cent. of the volume of carbon dioxide taken. The liquid in the apparatus gave a strong reaction for formaldehyde, and also a faint iodoform reaction.

II. Volume of $CO_2 = 266$. Volume of $H_2 = 379·5$.

The wire was maintained almost at a white heat for 15½ hours. The contraction, after cooling, was found to be 250 volumes, which is 93·9 per cent. of the volume of carbon dioxide taken. The liquid in the apparatus contained appreciable quantities of formaldehyde. Two duplicate experiments gave similar results.

Experiment with Carbon Monoxide, Hydrogen, and Steam.

Having satisfied ourselves that a mixture of moist carbon monoxide and hydrogen yielded very little aldehyde, whereas a mixture of carbon dioxide and hydrogen gave an appreciable quantity, some reason had to be found for the difference. It was thought that the main cause of the discrepancy might lie in the constant production of water in the latter case, which would aid in the removal of the freshly formed aldehyde. The experiment was therefore modified in one particular. Before introducing the carbon monoxide and hydrogen, a small test-tube containing water was suspended from *D D′* immediately above the heated wire *E*, which served to heat the test-tube and slowly evaporate the water contained in it.

The yield of formaldehyde obtained in one experiment performed in this way was materially increased.

Volume of $CO = 328$. Volume of $H_2 = 206$.

The heating was continued for 3 hours, during which time a small expansion of 10 mm. was observed. In spite of the short duration of the experiment, the condensed water contained a comparatively large amount of formaldehyde.

Experiments with Carbon Monoxide and Steam.

As might be expected from the result obtained with carbon monoxide, hydrogen, and steam, an appreciable quantity of formaldehyde was produced when the gases did not initially contain hydrogen. Two experiments were performed, both yielding similar results.

I. Volume of CO = 381.

The wire was heated for 4½ hours, and on cooling it was found that the gases had expanded 34/381ths of the original volume of the carbon monoxide. The liquid in the globe contained a comparatively large quantity of formaldehyde.

II. Volume of CO = 383.

The heating was continued for 18½ hours. The expansion was 46/383rds of the volume of carbon monoxide taken. An intense colour was obtained with Schiff's reagent.

Conclusion.

This work establishes the fact that, in the system containing carbon monoxide, hydrogen, water, and carbon dioxide, formaldehyde is undoubtedly produced at high temperatures.

THE VICTORIA UNIVERSITY OF MANCHESTER.

XCVI.—*The Diazo-derivatives of the Monoacetylated Aromatic Para-diamines.*

By GILBERT THOMAS MORGAN and FRANCES MARY GORE MICKLETHWAIT.

A STUDY of the diazonium salts derived from camphor-β-sulphonyl-*p*-phenylenediamine and benzenesulphonyl-*p*-phenylenediamine showed that these substances readily gave rise to a new type of diazo-compound, of which benzenesulphonyl-*p*-phenylenediazoimide,

$$C_6H_4{<}\begin{matrix}N\cdot SO_2Ph\\ | \\ N_2\end{matrix},$$

is the simpler example.

The investigation has now been carried a step further with the object of ascertaining whether the condensation occurs with the sulphonyl derivatives of other para-diamines, and also whether any

change of this kind occurs when the sulphonyl complex is replaced by another acyl group.

The results indicated in the experimental part of this communication show that the reaction represented by the following equation:

$$RSO_2\cdot\overset{1}{N}H\cdot X\cdot\overset{4}{N}_2\cdot OH - H_2O = X\begin{matrix}\overset{1}{N}\cdot SO_2R \\ | \\ \underset{4}{N_2}\end{matrix},$$

is fairly general for aromatic para-diamines containing a complex of the type $RSO_2\cdot NH$, and altogether seven examples of this series have now been studied.

On the other hand, no indication could be obtained of the production of similar diazo-anhydrides with acyl-*p*-diamines containing formyl, acetyl, succinyl, and benzoyl groups, so that at present the fundamental reaction represented by the foregoing equation must be regarded as being restricted to the mono-acylated *p*-diamines having one RSO_2 residue.

The changes observed in the case of benzoyl-*p*-phenylenediamine are somewhat singular. The sparingly soluble hydrochloride of this base yields on treatment with nitrous acid a soluble diazonium salt, which does not give rise to an anhydride with concentrated aqueous sodium acetate. When, however, the concentrated diazo-solution is poured into cold aqueous potassium hydrogen carbonate, a very pale yellow, crystalline precipitate is produced, which consists of a sparingly soluble *diazonium carbonate* having the formula

$$C_6H_5\cdot CO\cdot NH\cdot C_6H_4\cdot N_2\cdot HCO_3.$$

This substance is quite stable in the dry state, and does not explode either on heating or by percussion. It evolves carbon dioxide on treatment with cold hydrochloric acid, and the solution yields the azo-compound, $C_6H_5\cdot CO\cdot NH\cdot C_6H_4\cdot N_2\cdot C_{10}H_6\cdot OH$, when poured into an alkaline solution of β-naphthol. When boiled with water or aqueous solutions of mineral acids, the diazo-complex is destroyed, and benzoyl-*p*-aminophenol, $C_6H_5\cdot CO\cdot NH\cdot C_6H_4\cdot OH$ (m. p. 205—207°), is obtained.

In a similar manner, when the acetic acid solution of the diazotised benzoyl-*p*-phenylenediamine is poured into cold aqueous sodium nitrite, a sparingly soluble crystalline, yellow *diazonium nitrite*,

$$C_6H_5\cdot CO\cdot NH\cdot C_6H_4\cdot N_2\cdot NO_2,$$

is deposited.

This compound resembles the diazonium carbonate in readily yielding azo-derivatives with the phenols and aromatic diamines, the facility with which this condensation occurs indicating that the salt is a true diazonium compound, in spite of its distinctly yellow hue. The

appearance of colour in this case is probably to be attributed to the presence of a nitrite ion rather than to any rearrangement in the configuration of the diazo-complex.

On subjecting the monoformyl and monoacetyl derivatives of *p*-phenylenediamine to a similar series of operations, these substances did not furnish insoluble carbonates, no precipitate being formed on pouring the diazo-solutions into aqueous sodium or potassium hydrogen carbonate. The diazo-solution of the acetyl derivative (*p*-aminoacetanilide), when treated with aqueous ammonia, gave rise to a bulky brown precipitate, which, when washed with water and dried on porous tile, had the properties of, and gave analytical numbers corresponding with, the nitrosoamine, $CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot NH \cdot NO$. When dissolved in aqueous alkali and treated with β-naphthol, no azo-derivative was produced, the formation of the compound,

$$CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot N_2 \cdot C_{10}H_6 \cdot OH,$$

taking place only when the nitrosoamine is first dissolved in cold concentrated hydrochloric acid, and the diluted solution then added to an alkaline solution of the naphthol.

An attempt made to obtain a diazo-anhydride by treating an aqueous solution of *p*-aminoacetanilide hydrochloride with the calculated quantity of sodium nitrite and then adding aqueous sodium acetate led to the production of the diazoamino-compound,

$$CH_3 \cdot CO \cdot NH \cdot C_6H_4 \cdot N_2 \cdot NH \cdot C_6H_4 \cdot NH \cdot CO \cdot CH_3.$$

This substance could be crystallised from alcohol, whereas the foregoing nitrosoamine was decomposed on boiling with this solvent.

The results obtained with formyl-*p*-phenylenediamine were quite similar. Its diazotised solution yielded no insoluble compound either with sodium acetate or potassium hydrogen carbonate, but gave a brown precipitate of the nitrosoamine on treatment with ammonia. The hydrochloride of the formyl base, when diazotised and combined with a molecular proportion of the free base, gave rise to a diazoamine, which, however, was not obtained in a state of purity.

p-Aminosuccinanilic acid, $NH_2 \cdot C_6H_4 \cdot NH \cdot CO \cdot C_2H_4 \cdot CO_2H$, which was obtained by reducing *p*-nitrosuccinanil and partially hydrolysing the resulting *p* aminosuccinanil, when diazotised in hydrochloric acid, yields a *diazonium chloride*, $CO_2H \cdot C_2H_4 \cdot CO \cdot NH \cdot C_6H_4 \cdot N_2 \cdot Cl, H_2O$. This salt crystallises from a fairly concentrated solution and is quite stable in the dry state; its aqueous solutions do not yield insoluble diazo-derivatives with aqueous sodium acetate, potassium hydrogen carbonate, and ammonia.

An attempt to prepare the diazoamine of benzenesulphonyl-*p*-phenylenediamine showed that the tendency to form the cyclic diazoimide inhibits the production of this derivative. A glacial acetic acid

solution of the diazonium chloride and the original base, when treated with aqueous sodium acetate, yielded merely a mixture of the diazoimide and uncombined benzenesulphonyl-*p*-phenylenediamine.

Experimental.

I. *Arylsulphonyldiazoimides of the Aromatic* p-*Diamines.*

(1) *Naphthalene-α-sulphonyl*-p-*phenylenediazoimide*,

$$C_6H_4\begin{cases}—N\cdot SO_2\cdot C_{10}H_7 \\ \quad | \\ —N{:}N\end{cases}.$$

Naphthalene-α-sulphonyl-p-*nitroanilide*, $NO_2\cdot C_6H_4\cdot NH\cdot SO_2\cdot C_{10}H_7$, was obtained by heating together for 3 hours 20 grams of *p*-nitroaniline, 17 grams of naphthalene-α-sulphonic chloride, and 100 c.c. of dry toluene, the solvent being then evaporated and the residue boiled with excess of sodium carbonate. The filtered solution was cooled, the precipitated nitroaniline removed, and the final filtrate acidified with hydrochloric acid. The precipitate, when thrice crystallised from alcohol, separated in lemon-yellow needles melting at 205—206°.

0·4695 gave 36·7 c.c. nitrogen at 19° and 747 mm. N = 8·84.
$C_{16}H_{12}O_4N_2S$ requires N = 8·56 per cent.

Naphthalene-α-sulphonyl-p-*phenylenediamine*,

$$NH_2\cdot C_6H_4\cdot NH\cdot SO_2\cdot C_{10}H_7,$$

was prepared by reducing the preceding compound (12 grams) with 10 grams of iron, 300 c.c. of water, and 4 c.c. of glacial acetic acid, the yield being 10·5 grams; it does not crystallise readily, being somewhat too soluble in the ordinary organic solvents; after two crystallisations from benzene, it separated in clusters of brown needles and melted at 175°.

0·2454 gave 21·1 c.c. nitrogen at 19° and 747 mm. N = 9·72.
$C_{16}H_{14}O_2N_2S$ requires N = 9·39 per cent.

The hydrochloride of the base is only sparingly soluble, but when suspended in water, cooled and treated with the requisite amount of sodium nitrite the salt dissolves and the solution, when filtered into an excess of aqueous sodium acetate, yields an insoluble cyclic diazoimide which, when washed successively with water, alcohol, and light petroleum, decomposes indefinitely * at 164—167°, sintering and darkening at about 120°.

* The decomposition points of these diazoimides vary considerably with the rate of heating.

0·1694 gave 20·5 c.c. nitrogen at 19° and 746 mm. N = 13·65.
0·1542 „ 0·1235 $BaSO_4$. S = 10·99.
$C_{16}H_{11}O_2N_3S$ requires N = 13·59 ; S = 10·35 per cent.

This cyclic compound dissolves in concentrated hydrochloric acid and the solution, when diluted and mixed with alkaline β-naphthol, gives an azo-compound which, as is usual in this series, separates in the form of its sparingly soluble alkali salt.

(2) *Naphthalene-β-sulphonyl*-p-*phenylenediazoimide.*

Naphthalene-β-sulphonyl-p-*nitroanilide,* prepared in the same manner as its α-isomeride, crystallises from benzene in yellow needles melting at 168—169°.

0·5706 gave 41·4 c.c. nitrogen at 21° and 761 mm. N = 8·28.
$C_{16}H_{12}O_4N_2S$ requires N = 8·56 per cent.

Naphthalene-β-sulphonyl-p-*phenylenediamine,* obtained by reducing the preceding nitro-compound in the manner just indicated, crystallises from ethyl acetate or acetone in reddish needles melting at 231—232°. The reduction should be carried out in about 1½ hours, more prolonged heating leading to the formation of tarry products.

0·2430 gave 20·0 c.c. nitrogen at 18·5° and 768 mm. N = 9·55.
$C_{16}H_{14}O_2N_2S$ requires N = 9·39 per cent.

The cyclic diazoimide was obtained by diazotising the preceding base in the usual way and treating the filtered solution with sodium acetate, when the product separated as a yellow, microcrystalline precipitate which, when washed successively with water, alcohol, and light petroleum and dried in the desiccator, decomposed violently at about 130°.

0·1170 gave 14·2 c.c. nitrogen at 18·5° and 745 mm. N = 13·72.
0·2137 „ 0·1618 $BaSO_4$. S = 10·40.
$C_{16}H_{11}O_2N_3S$ requires N = 13·59 ; S = 10·35 per cent.

The diazoimide dissolves in concentrated mineral acids to form a diazonium salt which combines with alkaline β-naphthol; the azo-derivative, after two crystallisations from glacial acetic acid, melted at 220°.

(3) *Benzenesulphonyl*-2 : 5-*tolylenediazoimide,*

CH_3 — C_6H_3 ring — $N·SO_2Ph$, linked through $N:N$.

Benzenesulphonyl-5-*nitro*-o-*toluidine,* $NO_2·C_6H_3(CH_3)·NH·SO_2Ph$, was first prepared by condensation in toluene, but the yield was so

poor (2 grams of product from 20 grams of the nitro-base) that this process was abandoned in favour of the following method.

The calculated amount (1 mol.) of benzenesulphonic chloride was added to 10 grams of the nitro-base dissolved in 30 c.c. of warm pyridine, and the mixture gently heated for $1\frac{1}{2}$ hours, and then cooled and extracted with cold hydrochloric acid. The insoluble portion was thoroughly washed with water and dissolved in aqueous caustic soda; the benzenesulphonyl compound was precipitated from the cooled filtered solution with hydrochloric acid, the yield being 17 grams. The reaction in concentrated pyridine solution is at first quite vigorous and is accompanied by a considerable rise of temperature; after two crystallisations of the product from dilute alcohol, amber-yellow, prismatic crystals were obtained melting at 157—159°.

0·5088 gave 43·0 c.c. nitrogen at 18° and 770 mm. N = 9·89.
$C_{13}H_{12}O_4N_2S$ requires N = 9·59 per cent.

Benzenesulphonyl-2 : 5-*tolylenediamine*, $NH_2{\cdot}C_6H_3(CH_3){\cdot}NH{\cdot}SO_2Ph$, obtained by reducing the preceding nitro-base in the usual way, crystallised from hot water in colourless, hair-like needles melting at 147°.

0·2347 gave 22·0 c.c. nitrogen at 20° and 769 mm. N = 10·85.
$C_{13}H_{14}O_2N_2S$ requires N = 10·68 per cent.

The cyclic diazoimide was prepared by mixing the base with cold concentrated hydrochloric acid, when it yielded at first a plastic mass which rapidly changed to the crystalline hydrochloride. Crushed ice was now added, the mixture diazotised with a slight excess of aqueous sodium nitrite, and the filtered solution treated with sodium acetate, when a precipitate was at once produced consisting of small, light yellow needles which decompose explosively at 163°.

0·1412 gave 18·8 c.c. nitrogen at 17° and 760 mm. N = 15·22.
0·2450 ,, 0·2186 $BaSO_4$. S = 12·27.
$C_{13}H_{11}O_2N_3S$ requires N = 15·38 ; S = 11·71.

The *azo-β-naphthol* derivative, when isolated by acid from its sodium salt, produced by dissolving the cyclic diazoimide in cold concentrated hydrochloric acid and adding the diluted solution to alkaline β-naphthol, crystallises in prismatic crystals and melts at 184—185°.

(4) *Benzenesulphonyl*-p-*xylylene*-2 : 5-*diazoimide*,

$N{\cdot}SO_2Ph$
CH_3 CH_3
$N{:}N$

Benzenesulphonyl-5-*nitro*-p-*xylidine*, $NO_2{\cdot}C_6H_2(CH_3)_2{\cdot}NH{\cdot}SO_2Ph$, was produced by condensing 10 grams of 5-nitro-*p*-xylidine (m. p.

142°) with benzenesulphonic chloride in about 50 c.c. of pyridine, removing the solvent with hydrochloric acid, extracting the residue with aqueous sodium hydroxide, and precipitating the filtered solution with mineral acid; it was crystallised twice from dilute alcohol, when it separated in yellow, prismatic crystals melting somewhat indefinitely at 160—163°.

0·2151 gave 17·2 c.c. nitrogen at 18° and 760 mm. N = 9·23.
$C_{14}H_{14}O_4N_2S$ requires N = 9·15 per cent.

The sodium derivative of this compound is sparingly soluble in aqueous sodium hydroxide, and separated in the course of the foregoing preparation in long, yellow needles, which dissolved again on warming the solution.

Benzenesulphonyl-p-*xylylene*-2 : 5-*diamine*,

$NO_2 \cdot C_6H_2(CH_3)_2 \cdot NH \cdot SO_2Ph$,

was prepared by reducing the corresponding nitro-compound by the method already adopted for its lower homologues; it crystallises from water in straw-coloured needles melting at 144—146°.

0·1724 gave 15·3 c.c. nitrogen at 20° and 767 mm. N = 10·23.
$C_{14}H_{16}O_2N_2S$ requires N = 10·14 per cent.

The diazoimide was produced by diazotising the acylated diamine in a dilute solution containing excess of hydrochloric acid, filtering from a very slight residue, adding aqueous sodium acetate cautiously until a faint yellow precipitate became permanent, filtering again, and finally precipitating with excess of the alkali acetate. The bright yellow diazoimide was somewhat viscous at first, but hardened on triturating with cold water; it decomposed explosively at 125—130°.

0·1876 gave 23·9 c.c. nitrogen at 19·5° and 771 mm. N = 14·83.
0·2434 „ 0·1980 $BaSO_4$. S = 11·17.
$C_{14}H_{13}O_2N_3S$ requires N = 14·63; S = 11·14 per cent.

The *azo-β-naphthol* derivative, prepared by dissolving the diazoimide in concentrated hydrochloric acid and filtering into an alkaline solution of β-naphthol, separates in the form of the sparingly soluble alkali salt, which is decomposed by glacial acetic acid, yielding the free azo-compound, which separates in prismatic needles, and after two crystallisations melted at 215°.

(5) *Benzenesulphonyl*-1 : 4-*naphthylenediazoimide*,

$N\cdot SO_2Ph$

N:N

The 4-nitro-α-naphthylamine required in this preparation was produced by the nitration of aceto-α-naphthalide in glacial acetic acid and the partial hydrolysis of the mixed 4- and 2-nitroaceto-α-naphthalides according to Lellmann and Remy's directions (*Ber.*, 1886, **19**, 797). The product of the latter operation, which consists of the required base and the unaltered 2-nitroaceto-α-naphthalide, was, however, resolved into its components simply by dissolving the mixture in just sufficient hot ethyl acetate and cooling the solution rapidly. In these circumstances, practically the whole of the acetyl derivative crystallises out, whereas the 4-nitro-α-naphthylamine remains in solution until the greater portion of the solvent has been distilled off, when it separates from the concentrated solution as an orange, crystalline precipitate melting at 187°. A diazotisation experiment showed that the base was almost entirely free from 2-nitroaceto-α-naphthalide, and after one crystallisation from alcohol it melted at 191—192° (Lellmann and Remy give 191°). The 2-nitroaceto-α-naphthalide, which separated from the dilute ethyl acetate solution, was also extremely pure; it melted at 199—200° (corr., m. p. 199°) and was shown by successive treatment with nitrous acid and alkaline β-naphthol to be practically free from any 4-nitro-α-naphthylamine. In our hands, this mode of separation gave much more satisfactory results than the process of separation with dilute alcoholic sulphuric acid employed by Lellmann and Remy (*loc. cit.*).

Benzenesulphonyl-4-nitro-α-naphthylamine, $NO_2\cdot C_{10}H_6\cdot NH\cdot SO_2Ph$, could not be prepared by heating its generators in toluene, but it was found that a fairly good yield was obtained by condensation in quinoline or pyridine, the more volatile medium being preferable. Ten grams of benzenesulphonic chloride (1 mol.) were slowly added to a solution of 10 grams of 4-nitro-α-naphthylamine in 40 c.c. of pyridine; a vigorous action ensued which was completed by boiling the mixture for one and a half hours. The product was extracted successively with dilute hydrochloric acid and aqueous sodium hydroxide and the filtered solution from the latter extraction acidified, when 17 grams of the benzenesulphonyl derivative separated; it was crystallised twice from water, when spherular aggregates of bright yellow, fern-like crystals were obtained, melting at 158°.

0·2079 gave 15·3 c.c. nitrogen at 19° and 762 mm. N = 8·48.

$C_{16}H_{12}O_4N_2S$ requires N = 8·53 per cent.

Benzenesulphonyl-1 : 4-naphthylenediamine, $NH_2 \cdot C_{10}H_6 \cdot NH \cdot SO_2Ph$, was prepared by reducing the foregoing nitro-compound, but the reduction proceeded less smoothly by the iron and acetic acid method than was the case with the corresponding benzene derivatives. In many experiments, indefinite tarry products were the only result, but ultimately the following mode of procedure led to a more satisfactory conclusion.

Four grams of the nitro-compound were dissolved in about 200 c.c. of hot alcohol, 8 grams of tin were introduced, and 25 c.c. of concentrated hydrochloric acid gradually added with shaking, the mixture being boiled until test portions on treatment with water no longer exhibited any yellow coloration. The liquid was then transferred to a basin, the residual alcohol evaporated off, and about 5 c.c. of concentrated hydrochloric acid added. The colourless precipitate thus obtained was collected at the pump, washed free from tin salts with concentrated hydrochloric acid and finally water, dissolved in dilute aqueous caustic soda and the acylated base precipitated from the filtered solution with dilute acetic acid.

0·2237 gave 18·2 c.c. nitrogen at 20° and 767 mm. N = 9·40.

$C_{16}H_{14}O_2N_2S$ requires N = 9·39 per cent.

The base crystallises from benzene in clusters of colourless needles and melts at 186—187°.

The cyclic diazoimide was prepared by suspending the diamine in excess (20 mols.) of concentrated hydrochloric acid, adding crushed ice, and diazotising with a slight excess of sodium nitrite. The sparingly soluble diazonium salt was collected, dissolved in a mixture of glacial acetic and concentrated hydrochloric acids and the solution filtered into aqueous potassium acetate. The yellow diazoimide, which separated immediately as an amorphous, yellow powder, was collected and washed successively with water, alcohol, and light petroleum.

0·1849 gave 21·1 c.c. nitrogen at 20° and 769 mm. N = 13·22.
0·2351 ,, 0·1705 $BaSO_4$. S = 9·94.

$C_{16}H_{11}O_2N_3S$ requires N = 13·59 ; S = 10·35 per cent.

All the diazoimides hitherto studied are extremely sensitive to light, and the foregoing naphthalene derivative seems in this respect to be even more readily affected than its benzenoid homologues.

It dissolves in a mixture of glacial acetic and concentrated hydrochloric acids, and the diluted solution, when added to alkaline β-naphthol, yields an *azo-derivative* which crystallises from glacial acetic acid and melts at 261°.

II.—*Action of Nitrous Acid on other Monoacylated (Formyl, Acetyl, Succinyl, and Benzoyl) Derivatives of* p-*Phenylenediamine.*

(1) *Acetyl*-p-*phenylenediamine.*

The acetyl-*p*-phenylenediamine (*p*-aminoacetanilide) required in the following experiments was prepared from a specimen of *p*-nitroacetanilide kindly supplied by the firm of Messrs. Levinstein. A solution of this acylated diamine in dilute hydrochloric acid (3—5 mols.), when diazotised and added to concentrated aqueous sodium acetate, gave no precipitate corresponding with the diazoimides obtained from the arylsulphonyldiamines, neither was any insoluble product isolated by pouring the solution into concentrated aqueous potassium carbonate (compare the benzoyl derivative, p. 933). The addition of ammonia, however, gives rise to a voluminous brown precipitate which has the properties of a nitrosoamine,

$$C_2H_3O\cdot NH\cdot C_6H_4\cdot NH\cdot NO.$$

When collected, washed, and dried on porous tile it was found to dissolve in dilute acid or aqueous caustic alkali; the former solution at once gave the azo-condensation with alkaline *β*-naphthol, the latter only slowly. The compound could not be obtained in a crystalline form from the ordinary organic solvents. An estimation of nitrogen in the dried amorphous preparation agreed more closely with the percentage of a nitrosoamine than with that of a cyclic diazoimide or a diazoamino-compound.

0·1740 gave 35·2 c.c. nitrogen at 17° and 742 mm. N = 22·94.

$C_8H_9O_2N_3$ requires N = 23·47 per cent.

This substance decomposed somewhat indefinitely at about 85°.

A specimen of acetyl-*p*-phenylenediamine hydrochloride, obtained by passing hydrogen chloride into an acetone solution of the diamine, was dissolved in ice-cold water and treated successively with exactly one molecular proportion of sodium nitrite and excess of sodium acetate; a yellow precipitate was thus obtained, which decomposed suddenly at 195° and could be crystallised from alcohol, when it separated in small, brownish-yellow crystals decomposing somewhat indefinitely through a range of temperature from 190° to 200°. The substance retains water very tenaciously, its weight becoming constant only after prolonged heating in the steam oven.

0·1214 gave 24·3 c.c. nitrogen at 19° and 751 mm. N = 22·74.

$C_{16}H_{17}O_2N_5$ requires N = 22·50 per cent.

This result agrees with the formula for a diazoamine,

$$CH_3\cdot CO\cdot NH\cdot C_6H_4\cdot N_2\cdot NH\cdot C_6H_4\cdot NH\cdot CO\cdot CH_3,$$

which apparently indicates that only half the nitrite was required in the foregoing preparation. The compound was accordingly prepared by diazotising completely one molecular proportion of the hydrochloride suspended in moderately concentrated hydrochloric acid, and adding to the filtered solution excess of sodium acetate followed by one molecular proportion of the hydrochloride. The diazoamine separated immediately and this preparation decomposed at about 190° and resembled that obtained in the foregoing experiment. The substance is very sensitive to light, darkening rapidly on exposure.

(2) *Formyl*-p-*phenylenediamine* (p-*Aminoformanilide*).

This base was obtained by reducing with iron and dilute acetic acid formyl-*p*-nitroaniline, a substance formerly prepared by Osborn and Mixter (*Amer. Chem. J.*, 1886, 8, 346) by nitrating formanilide and described as melting at 187—194°; our specimen melted at 194—195° and gave the following numbers on analysis:

0·2448 gave 0·4514 CO_2 and 0·0881 H_2O. C = 50 29; H = 3·99.
0·2822 „ 41·8 c.c. nitrogen at 19° and 756 mm. N = 16·94.
$C_7H_6O_3N_2$ requires C = 50·60; H = 3·61; N = 16·86 per cent.

The acylated diamine crystallises from hot water in pale brown needles and melts at 125—127°. The crystallisation must be carried out rapidly, as the base quickly darkens if left in contact with the solvent. The hydrochloride, which is readily soluble in water, was prepared by saturating an acetone solution of the base with hydrogen chloride.

0·2074 gave 37·5 c.c. nitrogen at 20° and 748 mm. N = 20·36.
$C_7H_8ON_2$ requires N = 20·58 per cent.

When diazotised, it yields a solution from which neither sodium acetate nor alkali carbonates precipitate any insoluble diazo-derivative; ammonia, however, gives rise to a dark brown compound resembling the nitrosoamine obtained from the acetyl derivative (see p. 930). An ill-defined diazoamine, $COH\cdot NH\cdot C_6H_4\cdot N_2\cdot NH\cdot C_6H_4\cdot NH\cdot COH$, was obtained in the manner indicated for the acetyl diamine on p. 930; it was not, however, obtained crystalline, but when analysed in the crude state gave numbers approximating to the foregoing formula (N = 23·3, the calculated amount being 24·73 per cent.). The compound, when heated with cold mineral acid, undergoes the ordinary diazoamino-fission into its generators.

(3) p-*Aminosuccinanilic Acid* (*Succinyl*-p-*phenylenediamine*).

Succinanil (Menschutkin, *Annalen*, 1872, **162**, 182) was nitrated and the *p*-nitro-derivative (m. p. 205—208°) then separated from the ortho-isomeride, simultaneously produced by extracting out the latter with alcohol.

p-Aminosuccinanilic acid is conveniently obtained by suspending 4·4 grams of *p*-nitrosuccinanil in 100 c.c. of water and adding 1 gram of glacial acetic acid and 4 grams of iron filings, the metal being introduced gradually and the solution then boiled for 15 minutes. The mixture was rendered alkaline with 2 grams of anhydrous sodium carbonate, boiled for 8 minutes, and then filtered at the pump. The filtrate, when rendered neutral by the successive addition of acetic acid and powdered calcite, yielded the *p*-amino-acid, which was thus obtained in colourless needles melting at 183°, this melting point being identical with the temperature recorded by R. Meyer (*Annalen*, 1903, **327**, 39), who prepared the compound from *p*-phenylenediamine and succinic anhydride. *p*-Aminosuccinanil (m. p. 236°) is obtained by reducing the nitro-compound in the foregoing manner, excepting that the mixture is filtered immediately after the addition of the sodium carbonate, which in this case is added only in sufficient quantity to neutralise the acetic acid.

Succinyl-p-*aminobenzenediazonium chloride*,

$$CO_2H{\cdot}C_2H_4{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}Cl,H_2O,$$

was obtained on diazotising the amino-acid in a cold fairly concentrated solution in dilute hydrochloric acid; it is a perfectly stable compound, which burns quietly and does not explode on percussion.

0·1610 gave 21·0 c.c. nitrogen at 15° and 759 mm. N = 15·27.
0·3120 „ 0·1529 AgCl. Cl = 12·12.
$C_{10}H_{10}O_3N_3Cl,H_2O$ requires N = 15·32; Cl = 12·98 per cent.

The diazonium salt is readily soluble in water and its solution does not yield insoluble products with sodium acetate, alkali carbonates, and ammonia; when poured into moderately concentrated alkaline β naphthol, the alkali salt of the azo-β-naphthol is precipitated. This product, which readily dissolves in water, is decomposed by glacial acetic acid, yielding the free azo-β-naphthol derivative,

$$CO_2H{\cdot}C_2H_4{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH,$$

a substance which separates from glacial acetic acid as a crystalline powder and melts at 230—231°.

0·2300 gave 22·8 c.c. nitrogen at 18° and 768 mm. N = 11·58.
$C_{20}H_{18}O_4N_3$ requires N = 11·54 per cent.

(4) *Benzoyl*-p-*phenylenediamine* (p-*Aminobenzanilide*).

This compound, formerly obtained by Hübner (*Annalen*, 1881, **208**, 295) by reducing *p*-nitrobenzanilide with tin and hydrochloric acid, is readily prepared in quantitative yield from the nitro-compound by the iron and dilute acetic acid method of reduction. When the sparingly soluble hydrochloride is diazotised with sodium nitrite and hydrochloric acid, a soluble diazonium chloride is formed, the solution of which does not yield a precipitate with saturated aqueous sodium acetate. When, however, the solution is poured into cold aqueous sodium or potassium carbonate, a pale yellow, micro-crystalline precipitate is produced, which is only very sparingly soluble in cold water.

Benzoyl-p-*aminobenzenediazonium carbonate*,

$$C_6H_5 \cdot CO \cdot NH \cdot C_6H_4 \cdot N_2 \cdot HCO_3,$$

is a remarkably stable example of a diazo-carbonate, and may be dried in the water-oven without undergoing any appreciable change beyond a slight darkening in colour. The substance, although so stable in the dry state, could not be recrystallised, as it is decomposed on boiling with alcohol or water; in the former case, the replacement of the diazonium complex by hydrogen appears to take place, for the odour of acetaldehyde is very marked; with the latter solvent, the diazo-group is replaced by hydroxyl, and this change also occurs when the salt is boiled with aqueous mineral acid; the carbon dioxide evolved was in several instances absorbed in weighed soda-lime tubes, the percentage amount varying from 12·8 to 13·1 per cent., this being about 84 per cent. of the quantity calculated for the pure carbonate.

The *p*-hydroxybenzanilide (*N*-benzoyl-*p*-aminophenol), produced by the decomposition of the diazo-compound by water, crystallises from water in colourless needles melting at 205—207°. This melting point, although differing considerably from the number (227·5°) given by Hübner (*Annalen*, 1881, **210**, 378), is identical with the constant recorded for the substance by Hantzsch (*Ber.*, 1891, **24**, 4042).

The diazonium carbonate dissolves with effervescence in cold concentrated hydrochloric acid, and the diluted solution, when introduced into alkaline β-naphthol solution, gave a practically quantitative yield of the azo-compound, the amount in two experiments being 124 and 128 per cent., whilst the calculated value is 128·8. A specimen of the carbonate prepared from carefully purified benzoyl-*p*-phenylenediamine furnished the following data on analysis:

0·1952 gave 25·5 c.c. nitrogen at 19·5° and 757 mm. N = 14·95.

$C_{14}H_{11}O_4N_3$ requires N = 14·73 per cent.

The diazonium carbonate is sensitive to light, but if kept in the

dark may be preserved unchanged for an indefinite time. When shaken up with cold water, the carbonate yields a solution having a very faint alkaline reaction to red litmus. It readily condenses with amines and phenols, the addition of alkali accelerating the change in the case of the latter compounds. The hydrochloride of its azo-derivative with α-naphthylamine dissolves in alcohol to an intense bluish-purple solution.

It was hoped that this product might, on account of its great stability, be employed in the application of azo-compounds to the printing of textile fabrics, but comparative dye tests showed that the colours of its azo-derivatives could not compare in brilliancy with those obtained from diazotised *p*-nitroaniline. In this connexion, the compounds with "R salt" and "chromotrope acid" were examined, and the insoluble azo-compound with β-naphthol was recrystallised and analysed.

*Benzoyl-*p*-aminobenzeneazo-β-naphthol*,

$$C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}C_{10}H_6{\cdot}OH,$$

when crystallised successively from glacial acetic acid and alcohol, separates as a micro-crystalline powder and melts at 211°. With concentrated sulphuric acid, it develops a crimson coloration.

0·2808 gave 27·9 c.c. nitrogen at 20° and 767 mm. N = 11·47.
$C_{23}H_{17}O_2N_3$ requires N = 11·44 per cent.

*Benzoyl-*p*-aminobenzenediazonium Nitrite*,

$$C_6H_5{\cdot}CO{\cdot}NH{\cdot}C_6H_4{\cdot}N_2{\cdot}NO_2.$$

—The solution obtained by adding excess of sodium acetate to the hydrochloric acid solution of benzoyl-*p*-aminobenzenediazonium chloride, when treated with excess of sodium nitrite, yields a crystalline, yellow precipitate, which dissolves in water to an almost colourless solution.

0·2162 gave 39·0 c.c. nitrogen at 19° and 763 mm. N = 20·83.
$C_{13}H_{10}O_3N_4$ requires N = 20·74 per cent.

The aqueous solution of the diazonium nitrite, when treated with potassium iodide, does not liberate iodine until dilute acetic acid is introduced, when the liberation of the halogen occurs immediately. The diazonium salt condenses readily with phenols and aromatic amines, yielding azo-derivatives.

A solution of the diazonium nitrite or acetate, when poured into a saturated solution of sodium hydrogen sulphite, yields at first an orange-coloured precipitate, which rapidly changes to a pale yellow substance which is also sparingly soluble in cold water. The orange compound interacts at once with alkaline β-naphthol, whereas the

yellow product does not at first yield any azo-derivative; when, however, the mixture is kept for some time, a coloration is slowly developed.

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XCVII.—*Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds. Part III. Azo-derivatives of Symmetrically Disubstituted Primary Meta-diamines.*

By GILBERT THOMAS MORGAN and WILLIAM ORD WOOTTON.

UNTIL quite recently, considerable doubt has existed as to the precise action of a diazonium salt on a disubstituted meta-diamine of the general type

$$X\langle\overset{Y}{\bigcirc}\rangle NH_2, \quad (NH_2 \text{ below})$$

but in 1902 one of the authors showed that when the substituents (XY) were either 2Me, ClMe, or 2Cl an ortho-azo-compound was formed, although in smaller yield and less readily than when the condensation was effected with an isomeric base containing a free para-position with respect to one of the amino-groups. Moreover, the production of yellowish-brown azo-dyes on cotton fibres impregnated with diazotised primulin and treated with aqueous solutions of these symmetrically disubstituted bases showed that the diamines yielded azo-derivatives differing greatly in colour from the dyes obtained from their isomerides having a free para-position, the colour of the latter dyes having a reddish-brown shade similar in appearance to the colours obtained with the ordinary developers, *m*-phenylenediamine and 2 : 4-tolylenediamine (Trans., 1902, 81, 86).

This investigation has now been extended to the case of the meta-diamines containing nitro-groups and the heavier halogen atoms (bromine and iodide), in order to ascertain the influence of these substituents on the course of the condensations and the character of the products.

In the earlier experiments (*loc. cit.*, pp. 89 and 1384), it was shown that 4 : 6-dichloro-*m*-phenylenediamine showed less tendency to form

azo-derivatives than the similarly substituted bases, in which the two chlorine atoms are replaced by ClMe or 2Me, and on repeating the condensation with 4 : 6-dibromo-*m*-phenylenediamine this base was found to behave similarly, only indefinite non-crystallisable products being obtained with toluene-*p*-diazonium chloride, whilst the more stable *p*-nitrobenzenediazonium salt yielded a crystallisable azo-derivative.

With the object of completing this comparative study of the dihalogenated *m*-phenylenediamines, an attempt was made to prepare the di-iodo-compound.

Di-iodo-m-*phenylenediamine*, obtained in the manner indicated in the sequel, is a somewhat unstable substance darkening on exposure and decomposing at 83°. The orientation of the iodine atoms has not been determined, but by analogy with the dichloro- and dibromo-bases they should occupy the para-positions with respect to the amino-groups.

In its behaviour towards diazonium salts, the di-iodo-base resembles its chlorine and bromine analogues; with toluene-*p*-diazonium chloride, only indefinite products were obtained, whilst with the more stable diazo-compounds of the nitroanilines it gives rise to azo-derivatives giving numbers approximating to the formula $NO_2 \cdot C_6H_4 \cdot N_2 \cdot C_6H_3I_2(NH_2)_2$.

The three dihalogenated diamines yield azo-colours on fibres impregnated with diazotised primulin, and the shade produced deepens considerably as the atomic weight of the halogen increases.

These results indicate that the readiness with which these ortho-azo-compounds are formed is greatly influenced by the presence of nitro-groups in the molecule of the diazonium salt, and accordingly the diamines containing nitro-substituents were next examined with the object of ascertaining whether this group would exert a similar influence when present in the diamine nucleus.

5-Nitro-2 : 4-tolylenediamine (Tiemann, *Ber.*, 1870, **3**, 9), when coupled either with *p*-bromobenzenediazonium chloride or the diazo-compound from *p*-nitroaniline, gave good yields of azo-derivatives, and this influence of the nitro-group in the substituted diamines was further exemplified by a study of 6-*chloro*-4-*nitro*-m-*phenylenediamine* and the corresponding bromo-base.

The former of these bases was prepared either by chlorinating diacetyl-4-nitro-*m*-phenylenediamine or by nitrating diacetyl-4-chloro-*m*-phenylenediamine and then hydrolysing the products, these two alternative processes determining the orientation of the two substituents:

NH_2 NH_2 NO_2 $\xrightarrow{Cl_2}$ Cl NH_2 NH_2 NO_2 $\xleftarrow{HNO_3}$ Cl NH_2 NH_2.

The constitution of the chloro-base has already been determined by converting it into 1 : 2 : 4-trichlorobenzene, whereas that of the nitro-base depends on its conversion into the following compounds : 3-amino-*p*-nitrophenol and 3 : 6-diaminophenol, the latter being proved to be an ortho-diamine by condensation with benzil (Barbaglia, *Ber.*, 1874, **7**, 1257 ; Bertels, *Ber.*, 1904, **37**, 2279).

In a similar manner, the orientation of the substituents in 6-bromo-4-nitro-*m*-phenylenediamine was determined by preparing the base either by brominating diacetyl-4-nitro-*m*-phenylenediamine or by nitrating diacetyl-4-bromo-*m*-phenylenediamine and hydrolysing the product in the ordinary way. The constitution of 4-bromo-*m*-phenylenediamine has already been determined by converting it into 1 : 2 : 4-tribromobenzene (Morgan, Trans., 1900, **77**, 1205).

Before the alternative methods of preparing these bases had been worked out, an attempt to ascertain the configuration of the chloro-nitro-base by the Sandmeyer reaction led to the production of *s*-tetra-chlorobenzene accompanied by a smaller amount of chloranil.

The former of these substances results from the now well-known transference, which occurs so frequently in the case of diazonium salts containing nitro-groups : $NO_2{\cdot}C_6H_2Cl(N_2Cl)_2 \longrightarrow$

$$Cl{\cdot}C_6H_2Cl(N_2Cl)(N_2{\cdot}NO_2) \longrightarrow C_6H_2Cl_4 + N_2 + NO_2.$$

The nitrogen peroxide is not evolved as such, but is used up in oxidising some of the *s*-tetrachlorobenzene to chloranil.

Both these disubstituted diamines condense with diazonium salts to form azo-derivatives, and they yield ingrain colours with diazotised primulin.

Experimental.

Action of Diazonium Salts on 4 : 6-*Dibromo*-m-*phenylenediamine.*

The 4 : 6-dibromo-*m*-phenylenediamine required in these experiments was obtained by brominating diacetyl-*m*-phenylenediamine in warm glacial acetic acid solution. An intermediate additive compound first appeared, which passed into diacetyl-4 : 6-dibromo-*m*-phenylenediamine on treatment with water or dilute aqueous alkali, the latter medium giving the cleaner product. The diacetyl derivative was hydrolysed with alcoholic potash or hydrochloric acid ; in the acid hydrolysis, the excess of alcohol was evaporated off, the base precipitated with ammonia and recrystallised from hot alcohol, when it separates in glistening, brown needles melting at 135°.

p-*Nitrobenzene*-2-*azo*-4 : 6-*dibromo*-m-*phenylenediamine*,

Br NH$_2$

$$C_6H_2{\cdot}N_2{\cdot}C_6H_4{\cdot}NO_2,$$

Br NH$_2$

is precipitated on adding a hydrochloric acid solution of *p*-nitrobenzenediazonium chloride to a cooled alcoholic solution of the dibromo-base. The product crystallises from ethyl acetate in small, deep red crystals with a green, metallic reflex; it melts at 213° and develops a crimson coloration with concentrated sulphuric acid.

0·2794 gave 41·22 c.c. moist nitrogen at 17° and 754 mm. N = 16·96.
$C_{12}H_9O_2N_5Br_2$ requires N = 16·83 per cent.

m-*Nitrobenzene-2-azo-4 : 6-dibromo-*m*-phenylenediamine*, obtained as a brick-red powder, resembles the preceding compound, but is less soluble in water, alcohol, and ethyl acetate; it gives a bluish-scarlet coloration with concentrated sulphuric acid.

o-*Nitrobenzene-2-azo-4 : 6-dibromo-*m*-phenylenediamine* was not obtained crystalline; it is readily soluble in benzene and separates in the form of a red powder melting with decomposition at 152°.

0·1536 gave 0·1407 AgBr. Br = 38·96.
$C_{12}H_9O_2N_5Br_2$ requires Br = 38·55 per cent.

With cold concentrated sulphuric acid, this azo-compound develops a purple coloration. Portions of the solutions of the three preceding azo-compounds in cold concentrated sulphuric acid, when poured on to ice and filtered into an alkaline solution of "R-salt," gave no colorations, thus indicating the absence of fission products derivable from a diazoamine. On treating an alcoholic solution of the dibromo-base with toluene-*p*-diazonium chloride, the liquid became intensely red, but no precipitate was formed. The product, when precipitated by brine solution, seemed to consist of unchanged base mixed with tarry products from which a definite azo-derivative could not be extracted.

*Di-iodo-*m*-phenylenediamine* [$2NH_2$ = 1 : 3, 2I = 4 : 6 ?].

A fairly pure specimen of *m*-phenylenediamine hydrochloride (18 grams) was dissolved in 40 c.c. of warm water together with 50 grams of crystallised sodium acetate, and to the solution were slowly added 51 grams of commercial iodine dissolved in 210 c.c. of hot alcohol. The mixture assumed a deep dull green colour and an extremely pungent odour was noticed. After 10 minutes, the supernatant liquid was decanted from the dark sediment into a large excess of water, in which at first appeared an oily, ochreous precipitate changing after a few minutes into a greenish-brown mass of felted, microscopic needles. The crystalline product, when recrystallised from benzene, separates in lustrous, yellow needles which, on exposure, rapidly become reddish-brown and finally black. Prolonged boiling with benzene caused the

decomposition of the substance; the recrystallised specimen darkened at 79°, melted at 81°, and decomposed at 83°, evolving iodine.

0·1444 gave 10·1 c.c. nitrogen at 19° and 746 mm. N = 7·89.
0·0912 „ 0·1196 AgI. I = 70·88.
$C_6H_6N_2I_2$ requires N = 7·77; I = 70·53 per cent.

The base is soluble in alcohol or ether to a brownish-green solution; its hydrochloride, produced by passing hydrogen chloride into the benzene solution, is decomposed by boiling water. The ordinary processes of acetylation and benzoylation did not lead to the production of characteristic derivatives.

s-*Diphenyldicarbamidodi-iodo*-m-*phenylenediamine*,

$C_6H_2I_2(NH·CO·NHPh)_2$,

prepared by adding excess of phenylcarbimide to a warm saturated benzene solution of the base, decomposes at 200—203°. As it is only very slightly soluble in the ordinary solvents, it was analysed in the amorphous condition.

0·2050 gave 17·2 c.c. nitrogen at 18° and 750 mm. N = 9·56.
$C_{20}H_{16}O_2N_4I_2$ requires N = 9·36 per cent.

The picrate of the di-iodo-base crystallises from alcohol in minute needles.

Azo-derivatives of Di-iodo-m-*phenylenediamine.*

p-*Nitrobenzeneazodi-iodo*-m-*phenylenediamine*,

$NO_2·C_6H_4·N_2·C_6HI_2(NH_2)_2$.

—This azo-compound was prepared in the usual way by coupling the di-iodo-base with diazotised *p*-nitroaniline in alcoholic solution, this mixture being subsequently diluted with water, when the product separated as a deep reddish-brown precipitate which, when dry, had a dark green reflex and melted at 209°. As solvents appeared to decompose this azo-derivative, it was analysed without further purification.

0·1908 gave 0·1801 AgI. I = 50·97.
$C_{12}H_9O_2N_5I_2$ requires I = 49·87 per cent.

This azo-compound develops a crimson coloration with concentrated sulphuric acid.

o-*Nitrobenzeneazodi-iodo*-m-*phenylenediamine* resembles its isomeride and was similarly prepared; it gave on analysis I = 50·86 per cent. This compound begins to decompose at 215° and develops a crimson coloration with concentrated sulphuric acid.

As in the case of its dichloro- and dibromo-analogues, the di-iodo-*m*-phenylenediamine did not give a definite azo-derivative with toluene-*p*-diazonium chloride, only tarry products being obtained.

Azo-derivatives of 5-Nitro-2 : 4-tolylenediamine.—The 5-nitro-2 : 4-tolylenediamine (m. p. 154°) was obtained by nitrating diacetyl-2 : 4-tolylenediamine in cold concentrated sulphuric acid and then hydrolysing the product with boiling 10 per cent. caustic soda, this hydrolytic agent giving a cleaner preparation than alcoholic hydrochloric acid.

p-*Nitrobenzene-3-azo-5-nitro-2 : 4-tolylenediamine,*

$$\overset{NO_2\ NH_2}{\underset{CH_3\ NH_2}{C_6H}}\cdot N{:}N\cdot C_6H_4\cdot NO_2.$$

—An alcoholic solution of the nitro-base when treated with p-nitrobenzenediazonium chloride and subsequently diluted with water yielded a light vermilion powder sparingly soluble in the ordinary organic media and insoluble in water. The product dissolves in hot quinoline or pyridine, but separates out in an amorphous state on cooling; it decomposes at 283° and develops a brown coloration with cold concentrated sulphuric acid. The yield of this substance is almost theoretical.

0·1643 gave 35·2 c.c. nitrogen at 16° and 768 mm. N = 26·0.

$C_{13}H_{12}O_4N_6$ requires N = 26·5 per cent.

—The solution in cold concentrated sulphuric acid when poured on to ice gave no indications of the fission products of a diazoamine.

p-*Bromobenzene-3-azo-5-nitro-2 : 4-tolylenediamine,*

$$\overset{NO_2\ NH_2}{\underset{CH_3\ NH_2}{C_6H}}\cdot N_2\cdot C_6H_4Br.$$

—This azo-derivative, produced by coupling the diamine with p-bromobenzenediazonium chloride in glacial acetic acid solution, rapidly separated in light red flakes which, when crystallised from hot glacial acetic acid, separated in circular discs showing a spherulitic structure (m. p. 207—208°); the yield is about 89 per cent. of the theoretical. The compound dissolved in concentrated sulphuric acid to an orange-brown solution which, on dilution, was shown to be free from the fission products of a diazoamine.

0·1422 gave 25·0 c.c. nitrogen at 20° and 765 mm. N = 20·25.
0·0976 ,, 0·0515 AgBr. Br = 22·46.

$C_{13}H_{12}O_2N_5Br$ requires N = 20·00 ; Br = 22·86 per cent.

p-*Bromobenzene-2-azo-4-nitro-*m-*phenylenediamine,*

$$NH_2\cdot\overset{NH_2}{\underset{NO_2}{C_6H_2}}\cdot N_2\cdot C_6H_4\cdot Br.$$

—This para-azo-derivative was prepared in the manner indicated in the preceding experiment, excepting that the product was precipitated by aqueous sodium acetate; the yield was about the same as that of the foregoing compound. The substance is soluble in alcohol, ethyl acetate, and benzene, but crystallises best from glacial acetic acid, being thus obtained in short, yellow prisms (m. p. 220—224°) with a blue reflex. It develops an intense red coloration with cold concentrated sulphuric acid, and the solution, when successively poured on to ice, filtered, and added to an alkaline solution of "R-salt," gave no azo-colour, thus indicating the absence of fission products of a diazoamine.

0·1555 gave 28·3 c.c. nitrogen at 18° and 764 mm. N = 21·13.

$C_{12}H_{10}O_2N_5Br$ requires N = 20·83 per cent.

The Halogen Derivatives of 4-*Nitro*-m-*phenylenediamine.*

The brominated diamine and the corresponding chloro-compound were produced by halogenating diacetyl-4-nitro-*m*-phenylenediamine. This nitro-derivative was prepared by dissolving 10 grams of diacetyl-*m*-phenylenediamine in 100 c.c. of concentrated sulphuric acid and slowly adding to the solution at −8° 5 c.c. of concentrated nitric acid (sp. gr. 1·51) mixed with 15 c.c. of concentrated sulphuric acid cooled to the same temperature; the mixture was stirred continuously, the operation lasting about 10 minutes. The product was poured on to ice, the precipitated nitro-compound collected at once and washed with cold water. If the product is left in contact with the diluted acids, much frothing occurs and the yield is greatly diminished.

4-Nitro-*m*-phenylenediamine, obtained by boiling the diacetyl derivative with 4 parts of 10 per cent. aqueous caustic soda for 15 minutes and crystallising the product from water, separated from this solvent in yellow needles which have a blue reflex and melt at 159°.

Diacetyl-6-*bromo*-4-*nitro*-m-*phenylenediamine*,

$NO_2{\cdot}C_6H_2Br(NH{\cdot}CO{\cdot}CH_3)_2$.

—The diacetyl-4-nitro-*m*-phenylenediamine, dissolved in the minimum amount of warm glacial acetic acid, was treated with bromine (1 mol.) dissolved in 4 parts of the same solvent; after a few minutes, the solution was diluted with water, when the bromo-derivative separated and was crystallised from glacial acetic acid; it separates in colourless, nodular aggregates melting at about 212°, and is sparingly soluble in the usual organic solvents, crystallising from hot water in minute prisms.

0·1501 gave 16·0 c.c. nitrogen at 18° and 762 mm. N = 12·34.

$C_{10}H_9O_4N_3Br$ requires N = 13·28 per cent.

This substance was prepared in quantities not exceeding 1 gram, inasmuch as the employment of larger amounts of material led to the formation of non-homogeneous products.

6-*Bromo*-4-*nitro*-m-*phenylenediamine*,

$$NH_2 \cdot C_6H_2(NH_2)(Br) \cdot NO_2,$$

is preferably produced from its diacetyl derivative by hydrolysis with alcoholic hydrochloric acid, since the action of caustic alkali, unless carefully regulated, gives rise to tarry products. The base, when set free with ammonia and recrystallised from alcohol, is obtained in long, golden-yellow needles melting at 189—191°; it is sparingly soluble in cold water and readily dissolves in alcohol.

0·1498 gave 22·5 c.c. nitrogen at 17° and 762 mm. N = 17·51.
0·1454 „ 0·1185 AgBr. Br = 34·68.
$C_6H_6O_2N_3Br$ requires N = 18·10; Br = 34·43 per cent.

A satisfactory yield of this base was also obtained by nitrating diacetyl-4-bromo-*m*-phenylenediamine in concentrated sulphuric acid at −5° and subjecting the product to alkaline hydrolysis. After recrystallisation, the substance melted at 190—191° and was found not to depress the melting point of specimens prepared according to the first method.

2 : 6-*Dibromo*-4-*nitro*-m-*phenylenediamine*.

Owing to the difficulty experienced in freeing the 6-bromo-4-nitro-*m*-phenylenediamine from unaltered nitro-base in the preceding bromination, an attempt was made to render the change complete by operating on the free base, 3—5 grams of which were dissolved in glacial acetic acid and treated with 1·1 c.c. of bromine also dissolved in the same medium. Heat was generated and an orange-coloured precipitate was formed immediately, hydrogen bromide being evolved. The mixture was added to water, treated with ammonia, and the product recrystallised from alcohol, when it separated in lustrous, yellow needles melting at 190—191°.

0·1406 gave 17·7 c.c. nitrogen at 21° and 754 mm. N = 14·21.
$C_6H_5O_2N_3Br_2$ requires N = 13·50 per cent.

This base is identical with the compound obtained by Jackson and Fiske by heating 3 : 4 : 5-tribromo-1 : 2-dinitrobenzene with alcoholic ammonia and described as melting at 189—190° (*Amer. Chem. J.*, 1903, **30**, 53—82).

Diacetyl-6-*chloro*-4-*nitro*-m-*phenylenediamine*,

$$NO_2 \cdot C_6H_2Cl(NH \cdot CO \cdot CH_3)_2.$$

—A solution of diacetyl-4-nitro-*m*-phenylenediamine, dissolved in the minimum amount of hot glacial acetic acid, was rapidly cooled to promote the formation of small crystals, and into the paste thus produced a slight excess of chlorine was passed. Heat was generated, hydrogen chloride was liberated, and the acetyl compound passed into solution. The liquid was decanted from a dark sediment into water, and after neutralising with sodium carbonate the chloro-derivative separated as a pale yellow, crystalline powder. A good yield was obtained, the product being sparingly soluble in the usual solvents. It separated from hot water as a bulky mass of white, felted needles melting at about 222°.

0·1372 gave 17·1 c.c. nitrogen at 18° and 762 mm. N = 14·49.
0·1279 ,, 0·0628 AgCl. Cl = 12·15.
$C_{10}H_9O_4N_3Cl$ requires N = 15·52; Cl = 13·07 per cent.

6-*Chloro*-4-*nitro*-m-*phenylenediamine*.—The foregoing acetyl derivative is readily soluble in seminormal caustic soda, and the free base, which separates out on boiling the solution, crystallises from alcohol in golden-yellow needles; it is sparingly soluble in cold water and melts at 189—191°.

The diacetyl compound of this base was also obtained by nitrating diacetyl-4-chloro-*m*-phenylenediamine in glacial acetic acid solution; the diamine produced by hydrolysis melted at 189—191° and did not depress the melting point of the foregoing preparation.

0·1052 gave 20·6 c.c. nitrogen at 21° and 760 mm. N = 22·30.
0·1170 ,, 0·0852 AgCl. Cl = 18·44.
$C_6H_6O_2N_3Cl$ requires N = 22·46; Cl = 18·93 per cent.

When a solution of this substance in glacial acetic acid is treated with bromine, it yields an orange precipitate which is probably 6-chloro-2-bromo-4-nitro-*m*-phenylenediamine.

p-*Bromobenzene*-2-*azo*-6-*bromo*-4-*nitro*-m-*phenylenediamine*,
$C_6H_4{\cdot}Br{\cdot}N_2{\cdot}C_6HBr(NH_2)_2{\cdot}NO_2$.
—This azo-compound was formed by adding a hydrochloric acid solution of *p*-bromobenzenediazonium chloride to a solution of the bromonitro-base in cold glacial acetic acid. On addition of crystallised sodium acetate, the compound was deposited in brick-red flocks. It separates amorphously from solvents and decomposes indefinitely above 170°. When treated with cold concentrated sulphuric acid, it gives an orange-red coloration.

0·1677 gave 25·2 c.c. nitrogen at 17° and 762 mm. N = 17·50.
0·0896 ,, 0·0796 AgBr. Br = 37·79.
$C_{12}H_9O_2N_5Br_2$ requires N = 16·87; Br = 38·55 per cent.

p-*Chlorobenzene*-2-*azo*-6 *chloro*-4-*nitro*-m-*phenylenediamine*,
$C_6H_4Cl\cdot N_2\cdot C_6HCl(NH_2)_2\cdot NO_2$.
—This substance was prepared in the usual manner, the chloronitro-base being in alcoholic solution. The azo-compound separated at once as a very bulky brick-red precipitate, having when dry a bluish streak. It is insoluble in water, moderately soluble in alcohol and ethyl acetate, readily so in glacial acetic acid. As in the case of the preceding bromo-compound, this azo-derivative could not be obtained crystalline; it melts at 214—216°.*

0·1492 gave 27·0 c.c. nitrogen at 20° and 765 mm. N = 21·00.
0·1254 ,, 0·1082 AgCl. Cl = 21·34.
$C_{12}H_9O_2N_5Cl_2$ requires N = 21·47 ; Cl = 21·78 per cent.

This azo-compound dissolves in cold concentrated sulphuric acid to an orange solution. This solution, and also the one obtained with the corresponding bromo-compound, when successively treated with ice, filtered, and added to a solution of "R-salt," failed to give any coloration, thus indicating the absence of fission products of a diazoamine.

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XCVIII.—*Influence of Substitution on the Formation of Diazoamines and Aminoazo-compounds. Part IV. 5-Bromo*-as(4)-*dimethyl*-2 : 4-*diaminotoluene.*

By GILBERT THOMAS MORGAN and ARTHUR CLAYTON.

IN the course of an investigation on the interaction of the completely alkylated meta-diamines with diazonium salts, one of the authors found that tetramethyl-4 : 6-diamino-*m*-xylene did not condense with these reagents, negative results being obtained both with the simpler diazo-derivatives of aniline and its nitro-compounds and also with diazotised primulin. This inactivity is certainly due to the presence of the substituents in the two para-positions with respect to the amino-group, for when one of these positions is still open, as in the case

* Owing to the insoluble and uncrystallisable character of the acetyl and azo derivatives of the chloronitro- and bromonitro-bases, and the consequent difficulty experienced in purifying these products, their melting points must be taken as being only approximately correct. For the same reason, the analytical results do not always exhibit such a close agreement with the calculated values as could be desired.

of the lower homologue, tetramethyl-2 : 4-diaminotoluene, the production of the azo-colouring matter takes place readily and quantitatively (Trans., 1902, **81**, 650).

Inasmuch as the dipara-substituted primary meta-diamines still give azo-derivatives, although less readily than those diamines containing one free para-position (Trans., 1902, **81**, 89), it became of interest to determine how far the alkylation of a dipara-substituted *m*-diamine may proceed before the production of azo-derivatives is quite inhibited. With this end in view, the authors have undertaken a study of *as*-dimethyl-2 : 4-diaminotoluene, and have prepared a bromo-

NH_2

derivative, $N(CH_3)_2\cdot\langle\quad\rangle\cdot CH_3$, substituted in the remaining para-

Br

position in order to compare the action of diazo-compounds on the two partially methylated bases. The constitution of the bromo-base was determined by the following series of operations.

The nitration of dimethyl-*p*-toluidine leads to the formation of 2-nitro-dimethyl-*p*-toluidine, $N(CH_3)_2\cdot\langle\quad\rangle\cdot CH_3$, the position of the nitro-

NO_2

group being fixed by the alternative method of preparing the dimethyl base by the direct methylation of 2-nitro-*p*-toluidine (Haibach, *J. pr. Chem.*, 1902, [ii], **65**, 246). Under certain conditions, the foregoing nitration gives rise to a dinitrodimethyl-*p*-toluidine, the details of this alternative change being more fully indicated in the experimental section (p. 947).

On reduction, the mononitro-base yielded *as*-dimethyl-2 : 4-diaminotoluene, which was isolated in the form of its acetyl derivative, $N(CH_3)_2\cdot C_6H_3Me\cdot NH\cdot CO\cdot CH_3$. This compound was brominated with one molecular proportion of bromine in glacial acetic acid, and the monobromo-derivative, $N(CH_3)_2\cdot C_6H_2MeBr\cdot NH\cdot CO\cdot CH_3$, hydrolysed, yielding the hydrochloride of bromo-*as*-dimethyl-2 : 4-diaminotoluene. The position assumed by the entrant bromine atom was ascertained by the following alternative method of preparation.

Aceto-*p*-toluidide was converted successively into 3-bromoaceto-*p*-toluidide and 3-bromo-*p*-toluidine. The bromo-base was now nitrated by Claus and Herbabny's method, which consists in slowly adding its nitrate to cold concentrated sulphuric acid (*Annalen*, 1891, **265**, 367).

The mononitro-derivative, $NO_2\cdot C_6H_2MeBr\cdot NH_2$ (m. p. 121°), thus obtained was then alkylated by heating its hydrobromide with methyl alcohol at 140—150°. Under these conditions, the chief product is the dimethyl base, $NO_2\cdot C_6H_2MeBr\cdot NMe_2$ (m. p. 38°), which is separated from a small amount of secondary base by means of acetic anhydride.

On reduction, the nitrodimethyl base yields a bromo-*as*-dimethyldiaminotoluene, which was characterised by its acetyl, benzoyl, and benzenesulphonyl derivatives, and found to be identical with the bromo-*as*-dimethyl-3 : 4-diaminotoluene described above.

By this mode of preparation the position of the bromine atom is determined, and as the position of the amino-group was fixed by the preceding process, the bromodiamine is thus shown to be 5-bromo-*as*(4)-dimethyl-2 : 4-diaminotoluene, this proof of its constitution being outlined in the following diagram:

NH_2, CH_3 ↗ NH_2, Br, CH_3 → NH_2, Br, NO_2 (?), CH_3 → NMe_2, Br, NO_2 (?), CH_3 ↘ NMe_2, Br, NH_2, CH_3

NH_2, CH_3 ↘ NH_2, NO_2, CH_3 → NMe_2, NO_2, CH_3 → NMe_2, (?)Br, NHAc, CH_3 ↗ NMe_2, Br, NH_2, CH_3

Before the above proof of the constitution of the bromo-base was worked out, several other attempts had already been made to demonstrate this point. One of these consisted in completing the methylation of the bromo-base and comparing the result with the product obtained by completely methylating 5-bromo-2 : 4-diaminotoluene (m. p. 104°). In this way we showed incidentally that the two bromo-2 : 4-diaminotoluenes described in the literature as melting at 104° and 107° are in reality identical. The latter was prepared by reducing either 5-bromo-2:4-dinitrotoluene (Greta, *Annalen*, 1875, **177**, 231) or 5-bromonitro-*p*-toluidine (m. p. 118°). The recorded difference in the melting points is probably due to the fact that the base really decomposes through a wide range of temperature from 103—107°, the exact point at which fusion occurs depending on the rate of heating. The base melting at 104°, which had been formerly obtained by Ruhemann (*Ber.*, 1881, **14**, 2659) by brominating dibenzoyl-2 : 4-diaminotoluene and hydrolysing the product, was made by this process for the purpose of comparison and also prepared more conveniently from diacetyl-2 : 4-diaminotoluene. The products from these four different preparations did not depress each other's melting points and when treated by the Sandmeyer process with cuprous bromide yielded 2 : 4 : 5-tribromotoluene.

When 5-bromo-*as*(4)-dimethyl-2 : 4-diaminotoluene is treated with the diazonium salt of *p*-nitroaniline or *p*-bromoaniline, or with diazobenzenesulphonic acid, an ill-defined uncrystallisable product is obtained which gives the reactions both of a diazoamine and of an aminoazo-compound. This diamine, like 5-bromo-2 : 4-diaminotoluene, gives with

diazotised primulin on the cotton fibre a brownish-red azo-colour of somewhat duller shade than that produced with *as*(4)-dimethyl-2 : 4-diaminotoluene.

Experimental.

Preparation of 5-Bromo-as(4)-*dimethyl-2 : 4-diaminotoluene.*

First Method: From 2-Nitrodimethyl-p-*toluidine.*—A solution of 100 grams of dimethyl-*p*-toluidine in 1000 grams of concentrated sulphuric acid was cooled to 0° and slowly treated with 100 grams of concentrated nitric acid (sp. gr. 1·42) mixed with 300 grams of concentrated sulphuric acid. The mixture was continually agitated during the operation, then allowed to remain for six hours, and subsequently poured into a large volume of ice-cold water and the solution neutralised with sodium carbonate. The solid product was then skimmed off the surface, washed, and extracted with alcohol, and the alcoholic solution allowed to crystallise. In this way, about 100 grams of the mononitro-base were obtained, its melting point being 37°. Haibach (*loc. cit.*), who obtained it by methylating 2-nitro-*p*-toluidine, gave its melting point as 35°.

In diluting the product of nitration with water, it is essential that the temperature should be kept as low as possible; otherwise further nitration takes place, and the nitro-compound produced is much less soluble in alcohol, and consists almost entirely of a dinitrodimethyl-*p*-toluidine. This compound crystallises from alcohol in scarlet scales melting at 103°; when allowed to separate slowly from this solvent, dark red needles are obtained having the same melting point.

0·2912 gave 46·6 c.c. nitrogen at 16° and 762 mm. N = 18·71.
$C_9H_{11}O_4N_3$ requires N = 18·67 per cent.

This peculiar behaviour of the nitration mixture finds a parallel in the changes which were observed by P. von Romburgh to take place when dimethylaniline is nitrated under similar conditions (*Proc. K. Akad. Wetensch. Amsterdam*, 1902, 2, 342). This investigator found that in concentrated sulphuric acid dimethylaniline interacted with only one molecular proportion of nitric acid, but that if excess of this reagent is present, the further nitration leading to the formation of the dinitrodimethylanilines, melting at 176° and 112°, occurs only after the sulphuric acid solution is poured into water. In our experiments, only one dinitrodimethyl-*p*-toluidine (m. p. 103°) was obtained, the additional nitro-group being added when the sulphuric acid solution of the mononitro-compound with excess of nitric acid is poured into water, so that the temperature rises to 30—40°. When the mixture was thoroughly cooled during the dilution and neutralisation, then

further nitration was prevented, and only the mononitro-base was obtained.

Preliminary experiments showed that tin and hydrochloric acid gave the best results on reducing 2-nitrodimethyl-*p*-toluidine, the yield of diamine obtained with iron filings, water, and acetic acid being only small. After reducing and removing the tin, the solution of the diamine hydrochloride was concentrated, rendered faintly alkaline with caustic soda, and then treated with excess of acetic anhydride. In this way, about 65—70 grams of the acetylated diamine could be obtained from 100 grams of the nitro-compound. After one crystallisation from water, the acetyl-*as*(4)-dimethyl-2 : 4-diaminotoluene separated in white needles melting at 135°.

Five grams of the acetyl derivative, dissolved in 50 c.c. of glacial acetic acid at 16°, were treated with 4·2 grams of bromine in 5 c.c. of the same solvent, and after one hour the mixture was poured into water and the solution rendered ammoniacal.

The precipitated acetylbromodiamine was crystallised from alcohol, when it separated in woolly crystals melting at 163°.

0·2175 gave 0·1514 AgBr. Br = 29·62.
$C_{11}H_{15}ON_2Br$ requires Br = 29·52 per cent.

The hydrolysis of the acetyl derivative was effected by boiling with concentrated hydrochloric acid, when on concentrating the resulting solution a somewhat deliquescent hydrochloride was obtained. The base, when set free with ammonia, separated at first as an oil which slowly solidified; when crystallised from light petroleum (b. p. 40—60°), it was obtained in pearly leaflets melting at 40°.

0·1428 gave 0·1166 AgBr. Br = 34·75.
$C_9H_{13}N_2Br$ requires Br = 34·89 per cent.

The compound darkens on exposure, the colourless crystals rapidly acquiring an intense violet tint.

Second Method: From 3-*Bromo*-p-*toluidine.*—Twenty grams of powdered 3-bromo-*p*-toluidine nitrate were slowly sprinkled into 150 grams of concentrated sulphuric acid at 0° (Claus and Herbabny, *loc. cit.*), the mixture being thoroughly stirred throughout the operation, then allowed to remain for 6 hours, and subsequently poured into ice-water and neutralised with sodium carbonate. The precipitated base, obtained in practically quantitative yield, when crystallised from alcohol, separated in golden-yellow crystals (m. p. 121°).

3-*Bromonitrodimethyl*-p-*toluidine.*

Attempts were made to methylate the foregoing nitro-base with dimethyl sulphate and with methyl iodide and caustic soda, but the products were not inviting.

A more favourable result was obtained by heating the hydrobromide (3 grams) of the base with 5 c.c. of methyl alcohol for 8 hours at 140—150°. The oily or semi-solid product was freed from excess of alcohol on the water-bath and treated with acetic anhydride to remove unaltered base or any secondary amine. The residue, when repeatedly crystallised from alcohol in not too concentrated solution, yielded at low temperatures well-defined, yellow needles melting at 38°.

0·2784 gave 0·2048 AgBr. Br = 31·30.
$C_9H_{11}O_2N_2Br$ requires Br = 30·86 per cent.

Reduction of 3-*Bromonitrodimethyl*-p-*toluidine.*

This operation was conveniently carried out with tin and hydrochloric acid, the tin removed, and the diamine isolated in the form of its acetyl derivative. This substance, when crystallised from alcohol, separated in woolly crystals melting at 163°; it did not depress the melting point of the acetyl derivative obtained by the alternative method of preparation (see page 948).

0·2067 gave 0·1433 AgBr. Br = 29·52.
$C_{11}H_{15}ON_2Br$ requires Br = 29·49 per cent.

2-*Benzenesulphonyl*-5-*bromo*-as(4)-*dimethyl*-2 : 4-*diaminotoluene* was prepared from the two specimens of 5-bromo-*as*(4)-dimethyl-2:4-diaminotoluene obtained by the foregoing alternative methods. The products, when crystallised from alcohol and water, each melted at 178—179°, and a mixture of the two had the same melting point.

2-*Benzoyl*-5-*bromo*-as(4)-*dimethyl*-2 : 4-*diaminotoluene* was obtained from both preparations of the brominated diamine; the two specimens melted at 177—178°, and a mixture of the two in equal proportions had the same melting point.

5-*Bromo*-2 : 4-*tolylenediamine.*

(i) *Preparation from* 5-*Bromo*-4-*nitro*-o-*toluidine.*

One part of 5-bromo-*o*-toluidine dissolved in 5 parts of cold concentrated sulphuric acid was slowly treated with a molecular proportion of nitric acid (sp. gr. 1·42), also dissolved in the same medium, the temperature of the liquid being kept below 3°. After 1 hour, the

product was poured into water, the mixture neutralised, the precipitated nitro-compound recrystallised from alcohol, and obtained in yellow crystals melting at 118°.

The nitro-base was reduced with iron filings and acidified water (HCl), the product neutralised with sodium carbonate, and the resulting diamine extracted with ether. This base, which crystallises from light petroleum (b. p. 80—100°), was obtained in lustrous needles and melted with decomposition at 104—107°.

(ii) *Preparation from the Acyl Derivatives of Tolylene-2 : 4-diamine.*

Dibenzoyltolylene-2 : 4-diamine, prepared from the diamine by the Schotten-Baumann reaction, was dissolved in glacial acetic acid and treated with bromine (1 mol.) diluted with the same solvent. The brominated product, when recrystallised from alcohol, was boiled for several hours with alcoholic hydrochloric acid, the solution being kept saturated by passing in dry hydrogen chloride. The product, when evaporated and rendered alkaline, yielded a small amount of lustrous needles melting at 104—107° and giving an acetyl derivative melting at 254°. The hydrolysis was rendered more complete by repeating the experiment under pressure at 140°.

The base was more readily obtained from diacetyltolylene-2 : 4-diamine by the foregoing process; when recrystallised, it also decomposed indefinitely at 104—107°.

(iii) *Preparation from* m-*Bromotoluene.*

m-Bromotoluene was readily obtained by treating an alcoholic solution of 3-bromo-*p*-toluidine sulphate with ethyl nitrite and gradually heating the mixture to boiling (compare Wróblewski, *Annalen*, 1873, **168**, 153). The brominated hydrocarbon obtained after evaporating off the solvent and distilling in steam was suspended in cold concentrated sulphuric acid and nitrated with concentrated nitric acid ($2\frac{1}{8}$ mols.) mixed with 3 volumes of sulphuric acid. The dinitro-compound, when reduced with tin and hydrochloric acid, yielded 5-bromo-2 : 4-tolylenediamine, which, when crystallised from light petroleum, separated in fine needles melting at 104—107° and yielded an acetyl derivative melting at 254°. These preparations did not depress the melting points of those obtained by the preceding method.

These results show that the same bromodiamine is obtained by the three different methods of preparation; its orientation was determined by dissolving it in hydrobromic acid at 80° in the presence of cuprous

bromide and adding the calculated amount of sodium nitrite. The product, when distilled in steam, gave 2 : 4 : 5-tribromotoluene (m. p. 111°).

Bromination of 4-*Nitro*-o-*toluidine.*

In the various attempts made to determine the relative positions of the substituents of 5-bromo-*as*(4)-dimethyl-2 : 4-diaminotoluene, the bromination of 4-nitro-*o*-toluidine was studied in the hope that a monobromo-derivative would be obtained identical with the product of the nitration of 5-bromo-*o*-toluidine, their identity fixing the relative positions of the bromine and nitroxyl constituents. However, on treating 4-nitro-*o*-toluidine with bromine in glacial acetic acid diluting the product with ice-water, and neutralising with sodium carbonate, a substance was obtained which, when crystallised from alcohol, melted at 103°, and was therefore not identical with 5-bromo-4-nitro-*o* toluidine (m. p. 118°).

Analysis showed that the new base was a dibromo-4-nitro-*o*-toluidine, $CH_3 \cdot C_6HBr_2(NO_2) \cdot NH_2$.

0·3307 gave 0·4000 AgBr. Br = 51·47.

$C_7H_6O_2N_2Br_2$ requires Br = 51·58 per cent.

This dibromo-base withstands to a remarkable extent the action of diazotising agents, nitrous acid, and amyl nitrite in the presence of a mineral acid, leaving it practically unaffected.

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XCIX.—*The Action of Hypobromous Acid on Piperazine.*

By Frederick Daniel Chattaway and William Henry Lewis.

The *N*-dichloro-derivative of piperazine was obtained some years ago by Schmidt and Wichman (*Ber.*, 1891, **24**, 3237), who also obtained, by the action of bromine water on the base, a substance which they regarded as the corresponding *N*-dibromopiperazine. The properties of this compound, however, were so dissimilar both to those of the chlorine derivative and to those of all compounds known to contain bromine attached to nitrogen that the constitution assigned to it appeared improbable. The action of hypobromous acid on piperazine has therefore been studied, as this in most cases replaces amino- or imino-hydrogen immediately by bromine. The action of hypobromous

acid on piperazine is somewhat exceptional, as the additive compound which has been assumed to be formed in other cases where this reagent acts on bases is here unusually stable. The compound obtained in the first instance appears to be an additive product of two molecules of hypobromous acid to one molecule of the base; this, however, by liberation of water undergoes a partial conversion into the *N*-dibromopiperazine, which, unlike most other compounds of this type, is able itself to combine with two molecules of hypobromous acid. The substance obtained by the action of excess of hypobromous acid on piperazine, and which probably is similar to, if not identical with, that obtained by Schmidt and Wichman, is consequently a mixture of hypobromous acid additive products of piperazine itself and of *N*-dibromopiperazine.

N-Dibromopiperazine can be obtained from this intermediate mixed additive product by the action either of dilute alkali hydroxide or of piperazine; it resembles in properties the *N*-dichloro-derivative obtained by Schmidt and Wichman, and also other similarly constituted *N*-bromo-derivatives. It is dangerously explosive. *N*-Dibromopiperazine differs, however, from most other compounds of this type in that it is able on treatment with excess of hypobromous acid to combine with two molecules of the acid to form a comparatively stable additive compound; the actions may be represented as follows:

$$HN{<}\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}{>}NH \longrightarrow \begin{matrix}H\\HO\\Br\end{matrix}{>}N{<}\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}{>}N{<}\begin{matrix}H\\OH\\Br\end{matrix} \longrightarrow$$

$$BrN{<}\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}{>}NBr \longrightarrow \begin{matrix}HO\\Br\\Br\end{matrix}{>}N{<}\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}{>}N{<}\begin{matrix}OH\\Br\\Br\end{matrix}$$

Action of Hypobromous Acid on Piperazine.

On adding a dilute aqueous solution of piperazine to an excess of a cooled solution of hypobromous acid containing no free bromine, a pale yellow solid at once separates, which, on filtering off, pressing between filter-paper, and rapidly drying in a vacuum over phosphoric oxide, is obtained as a soft, yellow, amorphous powder. This product cannot be recrystallised, as it does not dissolve without decomposition in ordinary solvents. When warmed with chloroform or acetic acid, although a part goes into solution, it is obviously with considerable decomposition, and bromine is freely evolved. Even in a vacuum over phosphoric oxide, it decomposes slowly, bromine being liberated. On heating, it decomposes explosively at about 72° without previously melting. A weighed quantity of a specimen prepared as above and

dried over phosphoric oxide for two hours was added to acetic acid containing an excess of potassium iodide; it slowly dissolved and iodine was liberated, which was titrated with standard sodium thiosulphate, the total bromine being estimated in another portion by Carius' method.

0·2942 liberated I = 31·9 c.c. *N*/10 I. Br as NBr,HOBr or $\frac{1}{2}$Br as Br_2 = 43·35.

0·4793 yielded 0·7210 AgBr. Total Br = 64·02 per cent.

These results and the fact that the substance when treated with dilute potassium hydroxide yields a pale yellow solution containing potassium hypobromite, potassium bromide, and piperazine, whilst *N*-dibromopiperazine is formed, as well as the circumstance that it varies considerably in composition according to the length of time taken in its preparation and drying, seem to show that this yellow substance is not a single individual, but a mixture of additive products of bromine and hypobromous acid with piperazine, the aminohydrogen of which has been partially replaced by halogen. It agrees in properties with the compound obtained by Schmidt and Wichman by the action of bromine water on piperazine, and is probably, if not identical, very similar in composition to that substance.

N-*Dibromopiperazine* (*Diethylenedibromodiamine*),

$$BrN<\begin{matrix}CH_2\cdot CH_2\\CH_2\cdot CH_2\end{matrix}>NBr.$$

This compound can be obtained from the yellow additive product previously described by the action of either dilute potassium hydroxide or an aqueous solution of piperazine.

On suspending the yellow substance in a 2 per cent. solution of potassium hydroxide, its colour changes to a much paler yellow, and if chloroform is added the solid now dissolves easily. On separating the chloroform solution and driving off the solvent, *N*-dibromopiperazine is left, whilst the aqueous alkaline residue is found to contain potassium hypobromite and bromide together with piperazine and a very small quantity of ethylenediamine.

A better yield is obtained by using, instead of potassium hydroxide, a weak aqueous solution of piperazine itself, the following procedure giving a very satisfactory result. The yellow moist solid filtered from the excess of hypobromous acid used in its preparation was suspended in water and placed in a separating funnel with a small quantity of chloroform. An aqueous solution of piperazine was then slowly added, shaking vigorously after each addition. The insoluble yellow substance gradually passed into solution and the

chloroform became yellow. When all the solid had disappeared, the chloroform containing the dissolved *N*-dibromopiperazine was separated, dried over calcium chloride, and the solvent driven off in a current of dry air. *N*-Dibromopiperazine was left as a beautifully crystalline yellow solid; it was then repeatedly crystallised from a mixture of chloroform and a little petroleum. It is readily soluble in chloroform and acetic acid, sparingly so in petroleum, and crystallises from the former in yellow, transparent, short, flattened prisms. When heated to 79—80°, it explodes with great violence without previously melting. The explosion of even a very small quantity in a capillary tube may be dangerous, and on several occasions shattered a small beaker containing oil in which the tube was being heated. It was analysed by the iodometric method in acetic acid.

0·2936 liberated I = 48·1 c.c. *N*/10 I. Br as NBr = 65·49.
$BrN\colon[CH_2\cdot CH_2]_2\colon NBr$ requires Br as NBr = 65·52 per cent.

The action of piperazine as well as of potassium hydroxide on the yellow additive product is accompanied by a slight decomposition of the base and the formation of a small quantity of ethylenediamine. This was shown by shaking the liquid remaining after the separation of the chloroform solution of *N*-dibromopiperazine with an excess of a solution of hypobromous acid. In addition to a large quantity of the previously described additive product, a small quantity of ethylenetetrabromodiamine (Chattaway, this vol., pp. 37, 382) was formed and could be extracted by chloroform. On evaporating off the chloroform and recrystallising the red, crystalline residue several times, characteristic orange-red prisms of ethylenetetrabromodiamine were obtained which melted at 62° and exploded violently a few degrees higher. Its identity was established by an analysis.

0·1962 liberated I = 41·5 c.c. *N*/10 I. Br as NBr = 84·56.
$C_2H_4N_2Br_4$ requires Br as NBr = 85·07 per cent.

Action of Hypobromous Acid on N-*Dibromopiperazine.*

N-Dibromopiperazine unites at once with hypobromous acid to produce a comparatively stable additive product. A quantity of *N*-dibromopiperazine was dissolved in chloroform and the solution shaken with a well-cooled solution of hypobromous acid free from bromine; a yellow solid, insoluble in water or chloroform, at once separated. This was filtered off, and after thoroughly washing with water and chloroform was pressed between filter-paper and dried for two hours over phosphoric oxide in a vacuum. A soft, amorphous, yellow powder was obtained somewhat darker in colour than that

obtained from piperazine, but otherwise much resembling it in appearance and properties. It was not soluble in ordinary solvents without decomposition and liberation of bromine, and although it did not undergo any noticeable immediate change while drying, when kept in a vacuum over phosphoric oxide for a few hours a slight liberation of bromine occurred. On suspending it in a dilute solution of potassium hydroxide, *N*-dibromopiperazine was regenerated and a solution containing potassium hypobromite obtained. On heating, it decomposed explosively, without previously melting, at about 72°.

0·2133 liberated I = 38·3 c.c. *N*/10 I. Br as NBr,HOBr or $\frac{1}{2}$Br as Br_2 = 71·8.

0·2700 yielded 0·4818 AgBr. Total Br = 75·94.

$BrN{:}[CH_2CH_2]_2{:}NBr,2HOBr$ requires total Br (all as NBr and as HOBr) = 73·02 per cent.

Owing to the ease with which the compound is decomposed with liberation of bromine, very exact analytical numbers could not be expected.

The total bromine obtained by Carius' method is somewhat higher than that obtained by titration, and seems to indicate that the hypobromous acid additive product is mixed with a small amount of a bromine additive product or that substitution has taken place to a slight extent, the former being the most probable alternative.

The mode of formation of the compound, however, and the fact that by the action of potassium hydroxide, *N*-dibromopiperazine and potassium hypobromite are obtained point to the formula

$$BrN{:}[CH_2CH_2]_2{:}NBr,2HOBr$$

being correct and to the compound being an additive product of two molecules of hypobromous acid to a molecule of *N*-dibromopiperazine.

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C.—*Tetramethylammonium Hydroxide.*

By James Walker and John Johnston, Carnegie Research Scholar.

It is remarkable that, notwithstanding the interesting properties displayed by the tetralkylammonium hydroxides, the free bases have never been isolated in any definite form, and that nearly all experiments in which they have played a part have been conducted with the crude solutions obtained by the action of moist silver oxide on the

solution of the corresponding iodide. It is, of course, well known that such a solution on evaporation in a vacuum yields a crystalline mass, but no attempt seems to have been made to separate the crystals in a form suitable for analysis. Victor Meyer and Jacobson, in their *Lehrbuch der organischen Chemie*, say on the subject: "Es darf nicht unerwähnt bleiben, dass Analysen der freien Hydroxyde bislang nicht vorliegen, dass demnach die Annahme einer Hydroxylgruppe vorläufig noch eine durch das Verhalten der Basen freilich sehr wahrscheinlich gemachte Hypothese einschliesst." In the present paper, the isolation of several hydrates of tetramethylammonium hydroxide is described, together with a new method for the preparation of this and similar compounds.

One occasionally finds statements in text-books and in original memoirs drawing attention to the great stability of the salts of tetralkylammonium hydroxides and to the great strength of the bases themselves, and referring the impossibility of separating the hydroxides from their salts by means of caustic alkali to one or other of these causes. That the hydroxides cannot be liberated from their salts in this way has little to do with either the stability of the salts or with the affinity of the bases themselves, but in reality depends on the relative solubility (or volatility) of the reacting substances. It is strange that this erroneous conception should have persisted so long, or even that it should have arisen, for Hofmann is perfectly clear and explicit about the point in his original paper describing the first of these bases (*Annalen*, 1851, **78**, 266).

Practically the preparation of tetramethylammonium hydroxide from its salts resolves itself into a question of solubility as follows. In general, the equation

$$NMe_4X + MOH = NMe_4OH + MX$$

will represent a real action proceeding nearly to completion if M, X, and the solvent are so chosen that all the substances except MX shall be soluble, or at least that MX shall be much less soluble than either of the original reacting substances. This principle was applied by Hofmann in his preparations with water as solvent. For M and X he chose either the pair Ag,I or Ba,SO_4, in both of which cases MX is practically insoluble in water.

It is clear that if the general application of the above principle is justifiable, tetramethylammonium hydroxide may be prepared from a tetramethylammonium salt by means of potassium hydroxide if we so choose X and the solvent that of the substances represented in the equation

$$NMe_4X + KOH = NMe_4OH + KX$$

all shall be soluble except KX. The condition is fulfilled if X is Cl

and methyl or ethyl alcohol the solvent, for tetramethylammonium chloride and hydroxide, as well as potassium hydroxide, are all soluble in either solvent, whilst potassium chloride is almost insoluble.

It was found that a cold concentrated solution of tetramethylammonium chloride in methyl alcohol, when mixed with a similar solution of caustic potash in the same solvent, yielded at once a copious precipitate of potassium chloride, the action being accompanied by disengagement of heat. When the precipitate of potassium chloride had been removed by filtration, the solution was found to contain tetramethylammonium hydroxide, with only a trace of chloride or of carbonate when the reacting substances were pure and in equivalent proportions.

The same reaction takes place when ethyl alcohol is used as solvent, and indeed yields a product containing even less chloride, owing to the smaller solubility of potassium chloride in ethyl than in methyl alcohol. This advantage, however, is counterbalanced by the drawback that the alcohol is discoloured by the strongly alkaline solutions, and yields a somewhat coloured hydroxide. It is inadvisable to employ either sodium hydroxide or tetramethylammonium iodide in the reaction, as the sodium salts are more soluble in alcohol than the potassium salts and the alkaline iodides more soluble than the corresponding chlorides.

The isolation of the hydroxide from the alcoholic solution was at first attended with considerable difficulty. When the solution is subjected to distillation under diminished pressure, the alcohol at first evaporates at a low temperature, but as the solution becomes more concentrated, the temperature of the liquid must be raised, until eventually at about 50° the tetramethylammonium hydroxide in the solution begins to decompose into trimethylamine and methyl alcohol. If the operation is stopped at this point, the liquid contains about half its weight of hydroxide, and the syrupy solution on cooling deposits some crystals which, however, are difficult to remove, and are contaminated with chloride. A crop of crystals obtained from such a solution seemed to contain methyl alcohol of crystallisation, the composition being represented approximately by the formula $NMe_4OH,2CH_3OH$. It was found that the separation of the tetramethylammonium hydroxide could be most easily effected by the addition of a sufficient quantity of water to permit of the formation of a crystalline hydrate. The mode of operation may be illustrated by the account of a preparation made when the conditions had been determined with some accuracy.

Forty grams of pure dry tetramethylammonium chloride, in a sample of which the chlorine had been accurately estimated by titration, were dissolved in 80 c.c. of absolute methyl alcohol; a filtered solution of

potassium hydroxide in methyl alcohol had previously been prepared, and its concentration determined by the titration of a known weight with acid. Of this solution, 83·8 grams containing 20·4 grams of potassium hydroxide were mixed with the solution of tetramethylammonium chloride. A white precipitate at once separated, and was filtered off after the mixture had remained for 1½ hours at the ordinary temperature. The mixing and filtration were carried out in a case with glass top and back, which contained quicklime and was furnished with holes in movable slides for the reception of the hands. By the use of this case, contamination by carbon dioxide was reduced to a minimum. For the filtration, a Buchner filter with very slight suction was employed, and the precipitate was washed with a few c.c. of methyl alcohol. To the clear filtrate were now added 45 c.c. of water, and the liquid was subjected to distillation under reduced pressure from a water-bath at 35°. After 2 hours, the distillation was interrupted, and a sample of the remaining solution removed for analysis. It was found that 0·53 gram of the solution contained 0·19 gram of tetramethylammonium hydroxide, and that 90 grams of distillate contained 30 grams of water. No odour of trimethylamine was perceptible. To the solution, 35 grams of water were added, and the distillation was continued for 1 hour. The solution, which weighed 77 grams, was now practically free from methyl alcohol, and titration of a weighed sample showed that it contained 30 grams of tetramethylammonium hydroxide, the theoretical yield being 32·4 grams. The solution, which had no odour of trimethylamine, was then transferred to a glass crystallising dish with ground overlapping lid. On cooling, it partially crystallised, and 15 grams of a crystalline hydrate were filtered off. After the filtrate had remained for some days in a desiccator, 15 grams more of the same hydrate were deposited. Both the first and second crops of crystals were free from chloride and from carbonate, and left no residue on ignition. The mother liquor, on continued evaporation, deposited further quantities of crystals, but these were not quite so pure.

The crystalline hydrate yielded the following results on titration and combustion :

0·176 gram contained 0·089 gram of anhydrous $NMe_4OH = 50·6$.
0·091 ,, ,, 0·046 ,, ,, $NMe_4OH = 50·5$.

NMe_4OH in $NMe_4OH,5H_2O = 50·3$ per cent.

0·3570 gave 24·9 c.c. moist nitrogen at 15° and 748 mm. N = 8·0.
0·1860 ,, 0·1822 CO_2 and 0·2085 H_2O. C = 26·7 ; H = 12·5.

$NMe_4OH,5H_2O$ requires C = 26·5 ; H = 12·7 ; N = 7·7 per cent.

The crystals thus consisted of a pentahydrate of tetramethylammonium hydroxide. When slowly deposited, the pentahydrate forms

long, interlacing needles, which are excessively hygroscopic and extremely avid of carbon dioxide. As far as possible, therefore, all operations involving the transference of it or of any other hydrate were carried out over quicklime inside the above-mentioned case. The pentahydrate fuses at 62—63° without the odour of trimethylamine being perceptible. In a desiccator over quicklime or phosphoric oxide, the pentahydrate slowly loses water at the ordinary temperature and pressure, the change being visible by the efflorescence of the crystals; *in vacuo*, the dehydration is much more rapid. Measurements of the vapour pressure of the pentahydrate in a Frowein differential tensimeter resulted as follows:

Temp.	8°	15°	25°	35°	40°	45°	50°	55°	58°
Mm. bromonaphthalene	2	4	6·5	14	21	32	44	65	85
,, mercury	0·21	0·43	0·7	1·5	2·3	3 5	4·8	7·0	9·2

The pentahydrate is very soluble in water, as the following figures show:

Temp.	Parts of pentahydrate dissolved by 100 parts of water.	Parts of tetramethylammonium hydroxide in 100 parts of solution.
0°	151	30
15	220	34·6
63	∞	50·3

The heat of solution of the pentahydrate in 30 parts of water was found in two experiments to be -2120 and -2170 cal. for the gram-molecule.

When the pentahydrate is dehydrated at temperatures above 40° but below 60°, it partially liquefies after a time, but, as dehydration proceeds, solidification again takes place. In this respect, the dehydration resembles that of the hexahydrate of ferric chloride between 30° and 32°. By careful dehydration at a comparatively low temperature, a trihydrate may be prepared apparently identical with a crystalline hydrate which separated, on cooling, from the mother liquors of a pentahydrate crystallisation which had been concentrated further *in vacuo*. Analysis of the latter preparation yielded the following results:

0·148 required 10·35 c.c. $N/10$ HCl for neutralisation. Anhydrous base = 63·6; $NMe_4OH,3H_2O$ requires 62·8 per cent.

0·0956 gave 0·1153 CO_2 and 0·1134 H_2O. C = 32·9; H = 13·2.

$NMe_4OH,3H_2O$ requires C = 33·1; H = 13·1 per cent.

The trihydrate melts at 59—60° and has a vapour pressure much lower than that of the pentahydrate, a pressure of 1 mm. of mercury being reached at about 45°.

Dehydration of the pentahydrate for four days at 35° and under 18 mm. pressure yielded a solid having the composition of the monohydrate, NMe_4OH,H_2O, when determined by titration. This monohydrate lost no water on being heated under the same conditions for five days longer. It decomposed without melting at 130—135° with formation of trimethylamine, and dissolved somewhat slowly in water with evolution of heat. Experiments on dehydration by means of quicklime and phosphoric oxide were conducted in sealed tubes evacuated by means of the mercury pump, but in no case was the anhydrous substance formed. Even if the dehydration were pushed to the point of decomposition, the residue always gave, on titration, numbers which corresponded closely with the formula NMe_4OH,H_2O. Two such tubes, allowed to remain for a year and a half at the ordinary temperature, gave solids which had the composition $NMe_4OH,1{\cdot}1H_2O$ and $NMe_4OH,1{\cdot}3H_2O$ respectively. It is thus apparently impossible to obtain tetramethylammonium hydroxide in the anhydrous state, as the monohydrate decomposes with formation of trimethylamine before a temperature is reached at which it has a perceptible vapour pressure of water.

As the amount of water in the hydrates was usually and most conveniently estimated by deducting from the weight of hydrate the amount of anhydrous hydroxide determined by titration with acid, some direct experiments were made to check the indirect method. A weighed quantity of hydrate was placed in the closed end of a long, narrow, glass tube, and was covered with a long layer of quicklime. The tube and its contents were weighed and attached by the open end to a soda-lime tube to protect the quicklime. The hydrate was then gradually heated to the temperature of decomposition of the hydroxide, the trimethylamine and methyl alcohol escaping in the form of vapour. The increase in weight of the tube and quicklime was equal to the weight of the water in the hydroxide. The method gave results in exact accordance with the indirect method by titration. For example, crystals found by titration to contain 46·7 per cent. of water gave 46·5 per cent. by the direct method.

In the proportion of water in its hydrates, tetramethylammonium hydroxide does not correspond with the inorganic alkali hydroxides, at least, as far as the hydrates stable at the ordinary temperature are concerned, except in the case of the monohydrate. Complex quaternary bases (those, for example, derived from some alkaloids) are, however, known to exist as pentahydrates, in this respect resembling tetramethylammonium hydroxide.

An estimation of the strength of the base by means of the velocity of saponification of methyl acetate in $N/80$ solution showed that it was somewhat weaker than sodium hydroxide. The velocity constants

obtained at 25° were 0·0106 and 0·0115 respectively, so that if the strength of sodium hydroxide is represented as 100, that of tetramethylammonium hydroxide, under the above conditions, will be represented by 92.

The method of preparation described in this paper has been applied to other tetralkylammonium hydroxides, of which it is hoped to give an account in the near future. The expenses of the research were defrayed by a grant from the Research Fund of the Society.

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CI.—*Tetrethylsuccinic Acid.*

By JAMES WALKER and ANNIE PURCELL WALKER.

CRUM BROWN AND WALKER (*Annalen*, 1893, **274**, 51; *Trans. Roy. Soc. Edin.*, 1893, **37**, 361) obtained, by the electrolysis of the potassium ethyl salt of diethylmalonic acid, an oil which was separable by fractional distillation into a more volatile portion consisting chiefly of ethyl ethylcrotonate and a less volatile portion, which, from analogy, was expected to contain the ethyl ester of tetrethylsuccinic acid. The latter fraction, however, did not, on hydrolysis with hydrobromic acid, yield tetrethylsuccinic acid, but a neutral substance, which had the composition and molecular weight of tetrethylsuccinic anhydride. Owing to the absolute neutrality of this substance and the resistance which it offered to the action of alkalis, it seemed scarcely possible that the substance could be an acid anhydride, and it was suggested that it might conceivably be a dihydroxyfurfuran derivative in which all the hydrogen had been replaced by ethyl groups. The present investigation was undertaken with the consent of Professor Crum Brown in order that the nature of this neutral product might if possible be elucidated.

Potassium ethyl diethylmalonate was prepared and electrolysed, as described by Crum Brown and Walker (*loc. cit.*), and from 350 grams of ethyl diethylmalonate, 160 grams of the oily product of electrolysis were obtained. For the preliminary separation of the oil into the two fractions, distillation in steam was on this occasion employed instead of distillation under the ordinary pressure, in order that the decomposition by heat might as far as possible be avoided. The less volatile residue from the steam distillation weighed 60 grams, a somewhat larger proportion than that previously obtained. This was fractionally distilled under 22 mm. pressure. A small quantity boiling

below 150° was rejected, and the remainder separated into three portions: (*a*) 150—170°, (*b*) the main portion 170—180°, (*c*) over 180°. Small quantities of each of these fractions were separately saponified by an equal volume of hydrobromic acid of specific gravity 1·78, with which they mixed freely. The mixture contained in a sealed tube was allowed to remain for some hours at about 30° and then heated for 10 hours at 110°. After cooling, an oily layer was found on the surface of the aqueous layer; these layers were separated and the oil repeatedly washed with water, during which process it partially crystallised in the separating funnel. The crystals and oil were finally transferred to a porcelain basin and heated on the water-bath in order to expel the ethyl bromide formed on hydrolysis. On cooling, the liquid residue solidified to a crystalline mass, which, after purification, yielded a substance melting at 85°, and exhibiting the other properties of the neutral compound previously obtained. From the main fraction, the weight of crude crystals obtained was nearly three-fourths of the weight of oil taken, that is, approximately the weight of tetrethylsuccinic anhydride obtainable by hydrolysis from the corresponding diethyl ester. The remainder of this fraction was therefore again distilled under reduced pressure in order to obtain the ester approximately pure for analysis; it practically all boiled below 175° under 25 mm. pressure, but the temperature rose during the entire distillation. The chief fraction, boiling at 168—172°/25 mm., was analysed with the following result:

0·1630 gave 0·4025 CO_2 and 0·1490 H_2O. C = 67·32; H = 10·15.
$C_{16}H_{30}O_4$ requires C = 67·13; H = 10·48 per cent.

The oil had thus the composition of the *diethyl tetrethylsuccinate*. Since it could not be saponified by means of alkali, a determination of the number of ethoxyl groups it contained was made by Hewitt and Moore's modification of Zeisel's method.

0·1282 gave 0·1906 AgI. C_2H_5O = 28·5.
$C_{12}H_{20}O_2(O{\cdot}C_2H_5)_2$ requires C_2H_5O = 31·5 per cent.

This result leaves no doubt that there are two ethoxyl groups in the molecule of the ester examined. It was observed that the neutral substance melting at 85° crystallised from the hydriodic acid solution at the termination of the analysis, crystals of the same substance being also found in the cooler portions of the condensing tube. The ester was found to have a sp. gr. 1·011 at 4°/4°.

As the proportion of neutral substance obtained from the least and most volatile fractions was less than that yielded by the main fraction, no attempt was made to purify the esters they contained, the whole of the oil which remained being hydrolysed with fuming hydrobromic acid.

The neutral substance which they yielded was purified by recrystallisation from boiling ligroin and finally from hot methyl alcohol. The melting point of the pure substance was found to be 86° (corr.). The substance, when heated in a test-tube to 150°, slowly vaporises and condenses in the form of large crystals in the cooler portions of the tube; at 270° it boils without decomposition. From a solution in aqueous alcohol, the substance separates on evaporation of the alcohol in extremely slender needles which sometimes attain the length of several inches. The aqueous liquid which remains holds practically nothing in solution and is absolutely neutral.

Notwithstanding the neutrality of the substance and its insolubility in aqueous alkalis under ordinary conditions, a set of experiments was made on the assumption that it was the anhydride of tetrethylsuccinic acid. Since anhydrides of substituted succinic acids react readily with aniline in benzene solution (Auwers, *Annalen*, 1896, **292**, 132), a solution of the neutral substance in benzene was left in contact with two equivalents of aniline during several days: the substance was recovered unchanged. It was, however, attacked by aniline and by toluidine when heated with these bases for several hours at 180°. As the most characteristic test for the anhydrides of succinic acid derivatives is the production of a fluorescein, a portion of the substance was heated for one hour at 180° with resorcinol and a little freshly-fused zinc chloride. The dark product, when treated with a dilute solution of caustic soda, yielded a deep yellowish-red solution with well marked green fluorescence. This behaviour afforded a strong indication that the neutral substance was in reality the anhydride of tetrethylsuccinic acid. An attempt to split the anhydride ring by means of sodium methoxide was completely successful. A small quantity of the substance was treated in the cold with two equivalents of sodium dissolved in absolute methyl alcohol. After the solution had stood for several hours at the ordinary temperature, the bulk of the methyl alcohol was evaporated off on the water-bath. On addition of water, nearly all passed into solution, and the addition of hydrochloric acid to the aqueous solution produced an oily precipitate, thus proving that a portion of the original substance had been converted by the action of the sodium methoxide into the soluble sodium salt of an insoluble or sparingly soluble acid. The experiment was now repeated at the boiling point of methyl alcohol. After about two hours' heating, the methyl alcohol was removed by evaporation, the salt dissolved in water, acidified, and the liberated acid at once extracted with ether. On evaporation of the ether, a liquid remained which slowly crystallised; the crystals obtained melted at 48° and were completely soluble in dilute alkali. A determination of the neutralising capacity of this acid substance gave the following result:

0·095 required 3·98 c.c. $N/10$ baryta solution: the equivalent of the acid was therefore 240.

Since hydrogen methyl tetrethylsuccinate is a monobasic acid with the equivalent 244, it was evident that sodium methoxide had acted on the anhydride by direct addition, giving the sodium methyl salt according to the equation

$$C_{10}H_{20}{<}{\begin{matrix}CO\\CO\end{matrix}}{>}O + NaO{\cdot}CH_3 = C_{10}H_{20}{<}{\begin{matrix}CO_2Na\\CO_2{\cdot}CH_3\end{matrix}},$$

which on acidification yielded *methyl hydrogen tetrethylsuccinate*,

$$C_{10}H_{20}{<}{\begin{matrix}CO_2H\\CO_2{\cdot}CH_3\end{matrix}}.$$

The ester acid was found to be practically insoluble in water and excessively soluble in all organic solvents, from which it invariably separated as an oil which crystallised on long standing. From a solution in aqueous alcohol it separated in the crystalline state on slow evaporation of the alcohol, but it was found that the crystals had no sharp melting point and contained a considerable proportion of anhydride, to which the methyl hydrogen salt had reverted during the process of recrystallisation. Further attempts at the purification of the acid ester by recrystallisation were therefore relinquished. A Hewitt-Zeisel determination of methoxyl yielded the following results:

0·1568 gave 0·1365 AgI. $CH_3O = 11{\cdot}5$. $C_{11}H_{21}O_3(O{\cdot}CH_3)$ requires $CH_3O = 12{\cdot}7$.

It was again observed that crystals of the anhydride separated from the hydriodic acid on cooling.

When heated in a melting point tube, methyl hydrogen tetrethylsuccinate melts at 46—48°, and the liquid decomposes slowly at 100° with evolution of gas. If the heating is continued to 120°, the decomposition is complete, and the solid obtained on cooling the liquid now melts at 85°. Above 100°, then, methyl hydrogen tetrethylsuccinate decomposes into the anhydride and methyl alcohol according to the equation

$$C_{10}H_{20}{<}{\begin{matrix}CO_2H\\CO_2{\cdot}CH_3\end{matrix}} = C_{10}H_2{<}{\begin{matrix}CO\\CO\end{matrix}}{>}O + CH_3{\cdot}OH.$$

The remainder of the anhydride was now converted into the sodium methyl salt by means of sodium methoxide, and experiments were undertaken to ascertain the best method for the complete saponification of the compound. It was found that by heating the sodium methyl salt with excess of a 20 per cent. aqueous solution of caustic potash on the water-bath for 6 hours a salt was obtained which, on

acidification, yielded a crystalline acid melting at about 140°. Attempts to recrystallise this acid were at first unsuccessful on account of the readiness with which it reverted in solution to the anhydride; it was finally purified by dissolving in the minimum amount of anhydrous ether, in which it is very soluble, and precipitating by the addition of light petroleum. The acid purified in this way melted sharply at 149° with evolution of gas (water vapour), the resolidified substance melting at 86°, the fusing point of the anhydride.

0·1052 gave 0·2399 CO_2 and 0·0930 H_2O. C = 62·21; H = 9·82.

$C_{12}H_{22}O_4$ requires C = 62·61; H = 9·56 per cent.

0·0372 required 9·82 c.c. $N/30$ caustic soda for neutralisation. Acid equivalent = 114; equivalent of $C_{10}H_{20}(CO_2H)_2$ = 115.

The acid has thus the composition and neutralising capacity of *tetrethylsuccinic acid.* It is very soluble in ether, easily soluble in ethyl alcohol, less so in methyl alcohol, and sparingly so in light petroleum. In water it is very sparingly soluble, 4000 parts of the solvent being required to dissolve 1 part of acid at 25°.

The solutions of the alkali salts of tetrethylsuccinic acid exhibit the following peculiarity in their behaviour towards phenolphthalein. The aqueous solution (although slightly alkaline to azolitmin) is neutral to phenolphthalein in the cold. On warming, however, the solution to which the phenolphthalein has been added assumes a deep pink colour, which disappears on cooling. On again warming, the colour reappears, and the transition from coloured to colourless, and *vice versâ*, may be repeated indefinitely. On account of the increased hydrolysing power of water with rise of temperature, this behaviour is *a priori* probable enough, but a similar investigation of a great many sodium salts of organic acids showed that the property when noticeable at all is only feebly marked, and not in any way to be compared with the striking changes shown by the sodium salt of tetrethylsuccinic acid. In view of the ease with which the acid decomposes into anhydride and water, it was thought that the phenomena observed might have their origin in a reversible decomposition favoured by rise of temperature, but no evidence of such a decomposition could be obtained. Most probably the change of alkalinity with variation of temperature is due to the dissociation constant of the acid having an unusually large negative temperature-coefficient.

A 3 per cent. solution of sodium tetrethylsuccinate is not precipitated by calcium nitrate solution in the cold; a precipitate appears, however, on warming. A cold saturated solution of the calcium salt gives, when warmed, a slight precipitate which redissolves on cooling. The strontium salt is less soluble than the calcium salt, and like it is

more readily dissolved by cold than by warm water; the barium salt is still less soluble. A solution of sodium salt of the above concentration is not precipitated either by hot or cold solutions of magnesium chloride; the zinc and lead salts under the same conditions separate as bulky precipitates. The cadmium salt is moderately soluble in cold water, and the solution gives a copious precipitate on heating which redissolves completely when the solution is cooled. A solution which was clear at the ordinary temperature became turbid at 40° and gave a large precipitate at 70°. After standing for some days at the ordinary temperature, a saturated solution of the cadmium salt deposited crystalline rosettes, and no longer exhibited diminished solubility with rise of temperature.

The aqueous solutions of the alkali salts are apparently stable, since after several months they showed no deposition of anhydride and no increase of alkalinity. The resistance offered by the anhydride to the action of alkalis is thus all the more remarkable. It has already been stated that under ordinary conditions the anhydride does not dissolve in aqueous solutions of alkalis to any appreciable extent. Prolonged action of concentrated alkaline solutions does, however, convert the anhydride into a salt of the acid. Thus a small quantity of anhydride, which was left in contact with a 30 per cent. aqueous solution of caustic potash at the ordinary temperature, was after six weeks partially dissolved. On acidification, the solution yielded a precipitate which melted at 149° and was therefore tetrethylsuccinic acid. Concentrated alcoholic potash in great excess was heated with the anhydride for 24 hours on the water-bath; the residue obtained on removal of the alcohol was completely soluble in water, and from the aqueous solution an oil was deposited on acidification which did not crystallise on standing. This oil had the properties of ethyl hydrogen succinate, so that the alcoholic potash apparently acted as a solution of sodium ethoxide, the potassium ethyl salt being formed by direct addition.

This extreme resistance of an acid anhydride to the action of alkalis is very uncommon, possibly unexampled in organic chemistry. Even acids, such as pyrocinchonic acid, which have no stable existence, but pass spontaneously into their anhydrides, are at once regenerated in the form of salts by the action of alkalis on the anhydrides. Moreover, these anhydrides dissolve in water to furnish solutions which are distinctly acid and have a measurable dissociation constant. The aqueous solutions must therefore contain some proportion of the substance in the form of acid, although only the anhydride is obtained on evaporation. The case presented by tetrethylsuccinic acid is quite different; notwithstanding the insolubility of the anhydride in alkalis,

the acid liberated from solutions of the salts is quite stable in the solid state, and passes into the anhydride only in solution, especially in aqueous solution, when the conversion seems to be complete.

The progress of the conversion of the acid into anhydride may be followed by determining the electrolytic conductivity of the solution from time to time. It was found that in a solution saturated at 25° half the acid disappeared in the course of two hours. In 9 hours at the same temperature, only 15 per cent. of the original amount of acid remained unchanged, and in two days all the acid had disappeared. The anhydride was liberated in the characteristic form of long and very delicate needles.

A determination of the affinity constant of the acid resulted as follows:

v.	μ.	100 m.	100 k.
889	171	46	0·044

The value of μ is given in terms of ohms, and the degree of dissociation is calculated on the basis of $\mu_{\infty} = 373$. No great degree of accuracy can be claimed for the number $K = 0·044$ obtained for the affinity constant, owing to the difficulty of purifying the acid, its sparing solubility, and the impossibility of keeping it unchanged in aqueous solution. The value is greater than that of the constant of tetramethylsuccinic acid, namely, $K = 0·033$, which is in accordance with the fact established by Walden, that the constants of the symmetrical diethylsuccinic acids are considerably greater than those of the corresponding dimethylsuccinic acids. Owing to the practical insolubility of the methyl hydrogen tetrethylsuccinate in water at 25°, an attempt to determine the affinity constant of this acid ester gave no definite result.

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CII.—*The Synthesis of Substances Allied to Epinephrine.*

By George Barger and Hooper Albert Dickinson Jowett.

In a previous communication (Trans., 1904, 85, 192) it was shown by one of us that the constitution of epinephrine (adrenaline), the active principle of the suprarenal gland, might be represented by one of the two following formulæ:

I.	II.
$C_6H_3(OH)_2 \cdot CH \cdot OH$	$C_6H_3(OH)_2 \cdot CH \cdot NHMe$
$CH_2 \cdot NHMe$	$CH_2 \cdot OH$

of which I was regarded as the more probable.

These views have since been confirmed by the work of Pauly (*Ber.*, 1904, **37**, 1387), Stolz (*Ber.*, 1904, **37**, 4149), and Friedmann (*Beitr. chem. Physiol. Path.*, 1904, **6**, 92), although the first-named author prefers formula II.

Although we have been unable to synthesise a substance having the constitutional formula I, we have obtained its methylene and dimethyl ethers having the formulæ $CH_2{:}O_2{:}C_6H_3 \cdot CH(OH) \cdot CH_2 \cdot NHMe$ and $(CH_3O)_2{:}C_6H_3 \cdot CH(OH) \cdot CH_2 \cdot NHMe$ respectively. As all attempts to isolate the corresponding dihydroxy-base by the decomposition of the ethers were unsuccessful, we desire to give an account of the synthesis and the properties of the compounds prepared.

The synthesis was carried out as follows: an aldehyde, either piperonal or methylvanillin, was treated with magnesium methyl iodide and thus converted into the secondary alcohol, which, by loss of water, yielded the corresponding styrene. By the addition of bromine to this substance, the dibromide was formed, which by treatment with aqueous acetone yielded the bromohydrin, this product being then condensed with methylamine and the required base thus produced.

The stages in the synthesis may be represented in the case of piperonal as follows:

$$CH_2{:}O_2{:}C_6H_3 \cdot CHO \rightarrow CH_2{:}O_2{:}C_6H_3 \cdot CH(OH) \cdot CH_3 \rightarrow CH_2{:}O_2{:}C_6H_3 \cdot CH{:}CH_2 \rightarrow$$

$$CH_2{:}O_2{:}C_6H_3 \cdot CHBr \cdot CH_2Br \rightarrow CH_2{:}O_2{:}C_6H_3 \cdot CH(OH) \cdot CH_2Br \rightarrow CH_2{:}O_2{:}C_6H_3 \cdot CH(OH) \cdot CH_2 \cdot NHMe.$$

The constitution of the base produced was proved by its oxidation to piperonylic or veratric acid respectively. Although we were unable to isolate the dihydroxy-base, indications of the formation of a substance having the chemical and physiological properties of epinephrine were

obtained by the action of dilute hydrochloric acid at 150° on the methylene ether.

On attempting to carry out this synthesis with vanillin and protocatechuic aldehyde, it was found that these substances did not react with magnesium methyl iodide to give the required styrene. Consequently the synthesis could not be conducted on these lines.

Mameli (*Gazzetta*, 1904, **34**, [i], 358) has described a dibromide resulting from the action of bromine water on the styrene, but as this was not identical with the dibromide isolated by us, we repeated his experiments and found that the dibromide described by him is really a bromodihydrin, $CH_2{:}O_2{:}C_6H_2Br{\cdot}CH{\cdot}OH{\cdot}CH_2Br$. We also obtained this compound from the dibromide, $CH_2{:}O_2{:}C_6H_3{\cdot}CHBr{\cdot}CH_2Br$, by two distinct methods.

Experimental.

a-3 : 4-Methylenedioxyphenyl-aβ-dibromoethane,

O—CH₂ (structural formula: benzene ring with O—CH₂—O bridge, bearing CHBr—CH₂Br)

$$\begin{array}{c} O{-}CH_2 \\ |\quad\ \ | \\ C_6H_3{-}O \\ | \\ CHBr \\ | \\ CH_2Br \end{array}$$

This substance was obtained from the corresponding styrene, which was prepared from piperonal according to the method described by Klages (*Ber.*, 1903, **36**, 3595). In order to eliminate water from the secondary alcohol, it was found preferable to convert it first into the chloride, and then remove the elements of hydrogen chloride with pyridine.

3 : 4-Methylenedioxystyrene (20 grams) was dissolved in 20 c.c. of carbon disulphide, and to this a solution of bromine in carbon disulphide (1 gram per c.c.) was gradually added until a faint yellow colour was produced, the liquid being kept cool during the operation. A white, crystalline solid separated, which was collected and washed successively with carbon disulphide and light petroleum. It was recrystallised from carbon disulphide solution by the addition of light petroleum, and thus obtained in white, acicular crystals which melted at 82—83°.

0·1598 gave 0·1962 AgBr. Br = 52·2.

$C_9H_8O_2Br_2$ requires Br = 51·9 per cent.

α-3 : 4-Methylenedioxyphenyl-β-bromo-α-hydroxyethane,

O—CH₂ ring structure: $C_6H_3(O\cdot CH_2\cdot O)\cdot CH\cdot OH\cdot CH_2Br$

The dibromide was converted into the corresponding bromohydrin by dissolving it in acetone and then adding water to the acetone solution (compare Auwers and Miller, *Ber.*, 1902, **35**, 114); the liquid was left overnight and the acetone removed by evaporation, when the residue, together with the crystals which had separated, was extracted with ether, the ethereal solution washed with water and distilled. The final residue, which solidified, was recrystallised from hot dilute alcohol, the substance being thus obtained in long, acicular crystals which melted at 107—108°.

0·1758 gave 0·2872 CO_2 and 0·058 H_2O. C = 44·5 ; H = 3·7.
0·1229 „ 0·0923 AgBr. Br = 32·0.
$C_9H_9O_3Br$ requires C = 44·1 ; H = 3·7 ; Br = 32·6 per cent.

β-3 : 4-Methylenedioxyphenyl-β-hydroxyethylmethylamine,

$C_6H_3(O\cdot CH_2\cdot O)\cdot CH\cdot OH\cdot CH_2\cdot NHMe$

This substance was prepared by dissolving 4·9 grams of the bromohydrin in alcohol, adding 10 c.c. of an aqueous solution of methylamine (33 per cent.), and heating the mixture on a water-bath in a reflux apparatus for an hour. The alcohol was then distilled off, the residue dissolved in dilute hydrochloric acid, and extracted with ether to remove any unchanged bromohydrin.

The acid aqueous liquid was next rendered alkaline with sodium carbonate, evaporated to dryness, and the residue extracted with absolute alcohol; the alcoholic solution, after drying with potassium carbonate, left on evaporation a syrupy residue which could not be crystallised. The only crystalline salt obtained was the *picrate*, $C_{10}H_{13}O_3N,C_6H_3O_7N_3$, which was prepared by dissolving the syrupy base in dilute hydrochloric acid and adding a small quantity of an aqueous solution of picric acid. The liquid was decanted from the yellow oil which separated, and an excess of picric acid added. The

crystalline yellow substance, which slowly separated, was recrystallised, first from alcohol, and finally from water, being thus obtained in rosettes of yellow, acicular crystals melting at 178°.

0·1142 gave 0·189 CO_2 and 0·0408 H_2O. C = 45·1 ; H = 4·0.
0·0826 „ 10·2 c.c. nitrogen at 22° and 765 mm. N = 13·7.
$C_{16}H_{16}O_{10}N_4$ requires C = 45·3 ; H = 3·8 ; N = 13·2 per cent.

The *platinichloride*, prepared from the base in the usual way, was obtained as a yellow, amorphous powder having no sharp melting point ; the base employed in its production was obtained from the pure picrate by decomposition with potassium hydroxide and extraction with chloroform.

0·0686 gave 0·0166 Pt. Pt = 24·2
$(C_{10}H_{13}O_3N)_2,H_2PtCl_6$ requires Pt = 24·4 per cent.

When the base was oxidised with potassium permanganate at the ordinary temperature and the product worked up in the usual way, crystals of piperonylic acid (m. p. 227°) were isolated, thus proving the constitution of the base. An aqueous solution of the hydrochloride (2 per cent.) has a very slight physiological action, 0·02 gram, when injected into the jugular vein of a cat, producing a very slight rise (20 mm.) of blood pressure.

A number of experiments were made, both with the bromohydrin and the base, in order to decompose the ether and obtain the corresponding dihydroxy-derivative, but without success. When the base was heated with dilute hydrochloric acid at 150—160° for 6 hours, a solution was obtained which gave the catechol reaction with ferric chloride and sodium carbonate, and in very dilute solution gave a pink coloration with ammonia, rapidly turning brown, but no crystalline base could be isolated.

This solution, when injected into the jugular vein of a cat, gave a very marked rise of blood pressure, similar in some respects to that produced by epinephrine, but the amount of active substance present, if it was epinephrine, must have been very minute (approximately 0·005 gram from 2 grams of methylene ether).

On boiling the liquid with alkali and again testing, it was found to have lost its physiological action.

3 : 4-*Dimethoxystyrene*, $C_6H_3(O{\cdot}CH_3)_2{\cdot}CH{:}CH_2$.

This substance was prepared in a similar manner to the corresponding piperonyl compound by acting on methylvanillin with magnesium methyl iodide, and by withdrawing the elements of water by distillation from the secondary alcohol produced. The crude product distilled between 135° and 170° under 12 mm. pressure, but after several fractionations a liquid was obtained which boiled at 120—125° under 10 mm. pressure and proved on analysis to be the styrene.

0·1694 gave 0·4508 CO_2 and 0·1136 H_2O. C = 72·6 ; H = 7·4.
$C_{10}H_{12}O_2$ requires C = 73·2 ; H = 7·3 per cent.

The higher fraction consisted chiefly of methylvanillin.

a-3 : 4-*Dimethoxyphenyl-aβ-dibromoethane*, $C_6H_3(O{\cdot}CH_3)_2{\cdot}CHBr{\cdot}CH_2Br$.

This compound was prepared by the addition of bromine to the styrene by using ether as the solvent by a method similar to that employed in the case of the corresponding piperonyl compound ; it was obtained in white, acicular crystals which were purified by recrystallisation from benzene solution with the addition of light petroleum. The crystals melted at 102°.

0·1654 gave 0·1932 AgBr. Br = 49·7.
$C_{10}H_{12}O_2Br_2$ requires Br = 49·4 per cent.

The yield of dibromide, which was 18 per cent. of the methylvanillin employed, was much smaller than in the case of the corresponding piperonyl compound.

a-3 : 4-*Dimethoxyphenyl-β-bromo-a-hydroxyethane*,

$$C_6H_3(O\cdot CH_3)(O\cdot CH_3)\cdot CH\cdot OH\cdot CH_2Br.$$

This bromohydrin was prepared from the dibromide by the action of aqueous acetone; it formed long, acicular crystals, soluble in alcohol, ether, benzene, or carbon disulphide, but insoluble in water or light petroleum; it recrystallised most readily from carbon disulphide and melted at 68°.

0·1467 gave 0·1069 AgBr. Br = 31·0.
$C_{10}H_{13}O_3Br$ requires Br = 30·7 per cent.

The bromohydrin was converted into the methylamino-base by the method employed in the case of the piperonyl compound, but the product could only be obtained as a syrup which could neither be crystallised nor converted into any crystalline salt. When oxidised with potassium permanganate, it yielded veratric acid, melting at 179°.

A 2 per cent. solution had a similar physiological action to the corresponding piperonyl compound. When treated with dilute hydrochloric acid for 6 hours at 150—160°, the resulting liquid gave no catechol reaction with ferric chloride; the ether, therefore, had not undergone hydrolysis.

Composition of Mameli's Piperonyldibromide.—This substance was prepared according to the directions given by Mameli (*loc. cit.*), by the action of bromine water on the styrene. In addition to the compound described by him, a considerable amount of the bromohydrin (m. p. 108°) was obtained. The substance was twice crystallised from benzene and twice from alcohol; it then melted at 158° (Mameli gives 160°).

The same compound was produced by treating the bromohydrin with bromine water in direct sunlight. The yield was 60 per cent. of the theoretical.

0·1425 gave 0·1661 AgBr. Br = 49·6.
0·1442 „ 0·168 AgBr. Br = 49·6.
$C_9H_8O_3Br_2$ requires Br = 49·4 per cent.

Mameli's formula, $C_9H_8O_2Br_2$, requires Br = 51·9, and he found Br = 51·2 per cent. The results of the analyses together with the method of preparation, by directly brominating the bromohydrin, prove that the substance described by Mameli is not the dibromide but the dibromohydrin. This compound was also obtained in small

amount by the action of phosphorus pentachloride on the dibromide (m. p. 82°) in the attempt to split off the methylene group by the method which Fittig and Remsen used in the preparation of protocatechuic aldehyde from piperonal (*Annalen*, 1871, **159**, 148). The substance melted at 157—158°, and when mixed with an equal quantity of the dibromohydrin prepared as previously described, the melting point remained unchanged.

0·1355 gave 0·1681 CO_2 and 0·0308 H_2O. C = 33·8 ; H = 2·5.
0·1143 ,, 0·1306 AgBr. Br = 48·6.
$C_9H_8O_3Br_2$ requires C = 33·3 ; H = 2·5 ; Br = 49·4 per cent.

The formation of the dibromohydrin by phosphorus pentachloride is explained by the liberation of bromine which takes place in the first stage of the reaction, and the subsequent formation of the bromohydrin by the action of water on the halogen in the α-position.

Attempts were made also to prepare the styrene by distillation of the calcium salts of the corresponding methylenedioxycinnamic acid (compare Tiemann and Will, *Ber.*, 1881, **14**, 967). The product obtained was undoubtedly the styrene, as the dibromide was isolated, but the yield was so small (3 per cent.) that this method of preparation had to be abandoned.

The necessary physiological experiments in connection with this inquiry were performed by Dr. H. H. Dale, to whom we wish to tender our best thanks.

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CIII.—*Our Present Knowledge of the Chemistry of Indigo.*

By WILLIAM POPPLEWELL BLOXAM.

THE production of plant indigo being an industry of special importance in Bengal, the Government of this province has, for some years past, granted sums of money to enable scientific investigations to be carried on, with a view to effecting improvements in the cultivation and manufacture of this colouring matter; and the author was, in 1902, appointed to carry out experiments at the Dalsingh Serai Research Station with the co-operation of a biologist and an assistant chemist.

The results of these experiments have lately been printed by the Government of Bengal and issued as an official publication.*

In this report is set forth a sketch of the difficulties under which the cultivation and manufacture of plant indigo labour at present, together with suggestions as to the ways in which these difficulties may be removed. In the present paper the author excludes the treatment from the economic side and deals with the chemistry only.

Preliminary Experiments.

These experiments showed that it was altogether erroneous to regard as pure indigotin the various blue precipitates which can be obtained from aqueous extracts of the indigo plant. It was found that the precipitates obtained from aqueous extracts—(*a*) on oxidation in air, (*b*) on aërial oxidation in presence of ammonia, (*c*) on precipitation by chemical reagents—were in all cases greatly contaminated by admixture with other constituents derived from the plant. This fact is established by estimation of the nitrogen in the product, which in no case showed the numbers required for indigotin (N = 10·68 per cent.). It is suggested that indigotin, acting as a base, forms a series of lakes, from which the matter other than indigotin can only be removed with the greatest difficulty, in the wet way, by treatment with a series of solvents capable of extracting the foreign matter (see p. 980). The failure to recognise this property of indigotin accounts for the divergent yields attributed to the indigo plant itself and to the products obtained at the various stages of manufacture. For in all cases the earlier investigators have either (*a*) weighed the dried precipitate, assuming it to be pure indigotin, or (*b*) they have sulphonated the impure material, and have analysed the product by one or other of the current methods. Finding, therefore, that even with ready access to the fresh green plant it was not possible to prepare pure indigotin by precipitation in the wet way, the precautions taken by previous workers to obtain pure indigotin for use as a standard in establishing their analytical methods were subjected to a critical examination.

* "An Account of the Research Work in Indigo." Carried out at Dalsingh Serai Research Station (*under subsidy of the Government of Bengal*) from 1903 to March 1904. By W. Popplewell Bloxam, B.Sc. (Lond.), F.C.S., F.I.C., Research Chemist, H. M. Leake, M.A. (Cantab.), F.L.S., Biologist, with the assistance of R. S. Finlow, B.Sc., F.C.S., Assistant Chemist. (Calcutta: The Bengal Secretariat Book Depôt. 1905.)

Purification of Crude Indigo.

The methods employed for the purification of crude indigo may be subdivided, broadly, into four classes: *

(*a*) The treatment of crude cake indigo, or the synthetical product, with a series of solvents.

(*b*) The reduction of cake indigo, or the synthetical product, in alkaline solution; reoxidation, separation, and purification.

(*c*) Purification by sublimation.

(*d*) Purification by the use of volatile solvents.

Experience of wet methods *a*, *b*, and *d* shows that either the product obtained is not pure, or the yield is so small and the process so tedious that the production of even a few grams of the material is a practically impossible task.

In no case, also, does it appear that any crucial test was made of the purity of the final product obtained by these various methods. As stated previously (p. 975), the present author relies, at this stage, on the estimation of the nitrogen as the only test of purity.

Being dissatisfied with the methods previously recommended for the purification of crude indigo, the author spent some months in an unsuccessful search for a solvent, or mixture of solvents, which would dissolve indigotin selectively, to the exclusion of adherent foreign matters.

At this juncture, early in 1903, an abstract appeared (Abstr., 1903, i, 173) of a paper by A. Binz and A. Kufferath, entitled "Salts of Indigotin" (*Annalen*, 1902, **325**, 196), and on obtaining the full text of this paper it was seen that these authors had considerably extended our knowledge of the conditions of solution and of salt formation of indigotin.

In this paper, the following salts of indigotin are described:—indigotin hydrochloride, $C_{16}H_{10}O_2N_2,HCl$; indigotin hydrobromide, $C_{16}H_{10}O_2N_2,HBr$; indigotin platinichloride, $C_{16}H_{10}O_2N_2,PtCl_4$; indigotin monosulphate, $C_{16}H_{10}O_2N_2,H_2SO_4$; indigotin disulphate,

$$C_{16}H_{10}O_2N_2,2H_2SO_4.$$

These authors indicate that the monosulphate, being easily obtained and beautifully crystalline, should be employed in the purification of indigo, instead of the troublesome recrystallisation from glacial acetic acid or phthalic anhydride.

* A detailed account of the methods of analysis, together with a list of authors, will be found in Knecht, Rawson, and Lowenthal's *Manual of Dyeing* (Griffin: London), of which a new edition will shortly be issued.

The Preparation of Indigotin Monosulphate.

Binz and Kufferath's statement (*loc. cit.*) that indigo, when treated with a mixture of five volumes of glacial acetic acid and one of concentrated sulphuric acid, underwent no sulphonation even on the water-bath* was verified by the author, who then attempted the preparation of indigotin monosulphate.

Two specimens of indigotin were available for the purpose of the experiment, the first being the "B.A.S.F. Indigo pure," which is stated ("Chemistry of Pure Indigo," Badische Anilin- und Soda-Fabrik Brochure, 1900) to contain exactly 98 per cent. of indigotin.

The second specimen, which was purchased in Germany, was marked "100 per cent. Indigotin." For convenience, this sample will be designated "Indigotin by purchase."

The nitrogen value of each of these specimens of indigotin was determined by Kjeldahl's process, and the following results were obtained.

1. "*B.A.S.F. Indigo pure.*"—The mean of four estimations showed N = 9·82 (as against N = 10·68 per cent. contained in pure indigotin). This nitrogen value, calculated to indigotin (factor = 9·357), showed the true percentage of indigotin to be 91·88 instead of 98, as stated above.†

2. "*Indigotin by purchase.*"—In this case, the mean of four estimations gave N = 9·71. This nitrogen value, calculated to indigotin, indicated that the true percentage of indigotin was 90·85.

The specimen of "B.A.S.F. Indigo pure," which in reality contained only 91·88 per cent. of indigotin, was now treated with acetic-sulphuric acid (5 : 1 by volume), as recommended by Binz and Kufferath, and to the solution, after filtration, was gradually added an excess of ether. When left for one day, a fine crop of acicular crystals was obtained; these, which were collected and washed with ether until the washings showed only slight acidity, were then dried in a desiccator over sulphuric acid.

These crystals were found to be dissociated by water into sulphuric acid and indigotin, as stated by Binz and Kufferath. On dissociating

* Binz and Kufferath found, after completing their work, that the following statement occurred in Knecht, Rawson, and Lowenthal's *Manual of Dyeing* (London 1893. Vol. I. p. 327):—"Glacial acetic acid, containing a few drops of H_2SO_4, dissolves indigotin with a deep blue colour, and, on dilution with water, reprecipitates it unaltered." G. Watt, in his *Pamphlet on Indigo*, seems to give an earlier reference to the same observation originally attributed to Crookes.

† The accuracy of this result is confirmed by a statement, published later, by Möhlau and Zimmermann (*Zeit. Farb. Text. Chem.*, 1903, **10**, 189), in which they state that synthetical indigo contains 3—10 per cent. of a red dye-stuff.

a weighed portion of the crystals by boiling with water, washing the residue until free from acid, and titrating the filtrate and washings with standard alkali, the sulphuric acid found in two experiments was 23·97 and 23·71 per cent. respectively. Now, indigotin monosulphate, $C_{16}H_{10}O_2N_2,H_2SO_4$, requires $H_2SO_4 = 27·22$ per cent. The residues, after dissociation and washing free from acid, were ignited with sodium carbonate and shown to be free from sulphuric acid. These values, although not so good as those obtained by Binz and Kufferath ($H_2SO_4 = 27·00—28·02$ per cent.), raised no doubt that the salt obtained was the monosulphate. The deficiency in sulphuric acid was attributed to two causes:

(*a*) The ether used was not dry, and hence a slight hydrolysis of the crystals took place during the washing with this solvent, so that the final product contained free indigotin.

(*b*) The possibility of the red impurity present in the "B.A.S.F. Indigo pure" (see foot-note, p. 980) passing into solution in the acetic-sulphuric acid, and being precipitated with the crystals of monosulphate on the addition of ether.

It should be noted that Binz and Kufferath (*loc. cit.*) were more fortunate in being able to use, as the source of the monosulphate, a purified indigo powder supplied to them by the Badische Anilin- und Soda-Fabrik, which from their data contained 99·8 per cent. indigotin.

It now seemed clear that, if the acetic-sulphuric mixture were effectual in separating indigotin from its adherent impurities, it must fulfil the following conditions:

(*a*) Crude indigo must yield, when repeatedly subjected to solution in acetic-sulphuric acid, filtration, and hydrolysis by water, a residue of constant weight.

(*b*) This residue must yield 10·68 per cent. of nitrogen by Kjeldahl's method, this being the percentage of nitrogen in pure indigotin.

Experiments were now made to test these conditions, employing the two specimens "B.A.S.F. Indigo pure" (containing 91·88 per cent. of indigotin) and "Indigotin by purchase" (containing 90·85 per cent. of indigotin). The results showed that condition (*a*) was fulfilled, for, after repeating four times the operations of dissolving and hydrolysing, the residue was of constant weight.

The nitrogen values of the residues, however, were lower than that of indigotin, showing that these residues still contained some adherent impurity.

This impurity, which was soluble in acetic-sulphuric acid, was precipitated with the indigotin on hydrolysis by water, and presumably did not contain nitrogen.

The Red Colouring Matter (or Matters) of Plant Indigo.

Seeing that Binz and Kufferath's acetic-sulphuric acid method failed to purify the two samples of synthetical indigo, and that the failure seemed to be due to the presence of a red colouring matter in these specimens, and since, moreover, in plant indigo a red substance was also present which was held to be indirubin, it was determined to attempt the separation of the red matter from both plant and synthetical indigo, and to ascertain its nature and properties.

All authorities are agreed that indirubin (or indigo-red) is a constituent of ordinary plant indigo. Rawson (*loc. cit.*) gives directions for its extraction and some account of its properties. This method was adopted by the author for the treatment of cake indigo, with the exception that, after treatment with dilute hydrochloric acid, absolute methyl alcohol was employed instead of ordinary alcohol, the former being a better solvent for the red matter.

Accordingly some 200 grams of powdered Bengal cake indigo were extracted repeatedly with dilute hydrochloric acid (concentration 1 : 3) until the filtrate was only slightly brownish-red in colour. The residue was well washed with water and a considerable portion of the dry residue was then extracted in a Soxhlet's apparatus with absolute methyl alcohol, until the alcoholic extract showed that the blue colouring matter was beginning to pass into solution. The extraction was now discontinued and the main extract concentrated in a vacuum, one portion over solid caustic soda and the other over concentrated sulphuric acid. In both cases, a crystalline substance was deposited, which redissolved completely in methyl alcohol to a brilliant ruby-red solution.

Results of Tests applied to the Crystalline Residue.

(*a*) The solid, when treated with strong sulphuric acid, evolved some hydrogen chloride, but it could not be ascertained whether this was present as an integral constituent, or whether, as is more probable, the chloride was due to imperfect washing.

(*b*) The material contains no nitrogen, for negative results were obtained with the sodium test and also on ignition with soda-lime.

(*c*) Destructive distillation gave a heavy oily liquid distilling just in front of the flame, this distillate being faintly acid to litmus.

(*d*) The material is easily soluble in methyl, ethyl, and amyl alcohols and in chloroform, benzene, and toluene; it is insoluble in water, but is soluble in acetic-sulphuric acid (5 : 1), from which it is again deposited on dilution with water.

(*e*) It does not give a tannin reaction with ferric chloride, neither does it reduce Fehling's solution.

(*f*) It gives the fluorescein reaction which is said to be characteristic of phthalic anhydride and other anhydrides of dicarboxylic acids, as, for example, succinic anhydride.

The specimens of the synthetical product, "B.A.S.F. Indigo pure" and "Indigotin by purchase," were now similarly treated, and were found to yield a red colouring matter (or matters) which behaved towards reagents similarly to the product obtained from ordinary plant indigo.

From the foregoing experiments, it seems clear that there is a red colouring matter (or matters) common to both plant and synthetical indigo and that this red substance is not indirubin, for it contains no nitrogen.

The author hopes to be able in the future to ascertain the nature of this red substance. There seems at present to be no doubt as to the existence of indirubin, on the authority of Baeyer and other investigators; but apparently, through lack of careful examination of the red colouring matter occurring in synthetical and plant indigoes, the latter has been mistaken for indirubin by Rawson and others.

The author maintains that great importance attaches to the elucidation of the nature and function of the "red" in indigo manufacture both from the chemical and economic points of view (compare Report to the Government of Bengal, p. 21).

Explanation of the Failure of the Acetic-sulphuric Acid Method to yield Pure Indigotin.

The foregoing experiment demonstrates that the acetic-sulphuric acid dissolves not only indigotin, but also the non-nitrogenous red matter, which, on hydrolysis of the solution thus obtained, is precipitated together with the indigotin.

Thus a point is reached, after several solutions in the mixed acids and hydrolysis by water, when the precipitate maintains a constant weight and a constant degree of impurity. In consequence, Binz and Kufferath's method was abandoned,* and the following modification of the process was attempted.

Attempts to prepare Pure Indigotin from Ordinary Plant Indigo by Successive Extraction with Methyl Alcohol and Acetic-sulphuric Acid.

The author determined first of all to extract the "red" completely with absolute methyl alcohol, and then to apply to the residue the

* Möhlau and Zimmermann (*Zeit. Farb. Text. Chem.*, 1903, **10**, 189) state that they can obtain pure indigotin by a modification of Binz and Kufferath's process, but they give no nitrogen values for their product.

acetic-sulphuric acid method. Preliminary experiment showed that methyl alcohol dissolved the "red" without extracting the indigotin. For this experiment, some purified plant indigo was available, which had been standardised by Rawson and pronounced to contain 94·8 per cent. of indigotin.

Two estimations of nitrogen by Kjeldahl's process yielded N = 9·97 and 10·01, these values corresponding respectively with 93·29 and 93·66 per cent. of indigotin, or a mean value of 93·47.

Duplicate portions of the same specimen were now extracted until the red colouring matter was completely removed with methyl alcohol. The residues thus obtained were dried and then dissolved in hot acetic-sulphuric acid; the solutions were filtered through asbestos, and the filter washed free from blue with hot acetic-sulphuric acid. The clear filtrates and washings were poured in a thin stream into six times their volume of boiling water and thus hydrolysed. The precipitates were collected on tared filters and washed until free from acid. Drying was effected, first in the water-oven and finally at 105°, until the weight was constant. Only one solution in acetic-sulphuric acid and subsequent hydrolysis was made in each case, for the filtrate obtained after hydrolysis was practically colourless.

The results of the analyses are stated in apparent percentages of pure indigotin in the residues, (*a*) after one extraction with methyl alcohol, (*b*) after one extraction with acetic-sulphuric acid (5 : 1).

	I.	II.	Mean.
(*a*)	95·44	95·81	95·63
(*b*)	93·56	93·05	93·31

Grouping together the results of analyses of the same specimen of indigo obtained by different methods, one obtains the following data:

Method.	Percentage value of indigotin.
(1) Rawson's (not indicated)	94·8
(2) Based on estimation of nitrogen (Kjeldahl)	93·47
(3) By successive extraction with methyl alcohol and acetic-sulphuric acid (5 : 1)	93·31

The concordance between the results obtained by methods (2) and (3) seems all that could be desired, and afforded hope that here was available both a process for the purification of crude indigo and a method of analysis.

Analyses were next made of two specimens of ordinary Bengal cake indigo, employing successive extraction with acetic-sulphuric acid (5 : 1) and methyl alcohol. As the specimens contained presumably 70 per cent. or less of indigotin, solution in the mixed acids and

hydrolysis by water were performed twice, and the loss in weight determined at each stage.

In each case, the analyses were made in duplicate, and the moisture and ash were estimated.

Results of Analysis. No. I.

	Percentage results. (a)	(b)
Moisture (at 110°)	4·33	4·33
Ash	2·26	2·26
	Percentages recovered. (a)	(b)
After 1st extraction with acetic-sulphuric acid ...	77·76	78·34
,, 2nd ,, ,, ,, ,, ,,	74·92	75·34
After extraction with methyl alcohol	70·34	69·34
Indigotin [?] by direct weighing after extraction	70·34	69·34
True percentage of indigotin present (as calculated from the nitrogen value)	63·69	

To test the purity of these products, (*a*) and (*b*), after the foregoing extraction, they were intimately mixed and nitrogen estimations made by Kjeldahl's method, but the mean result obtained was N = 9·74 per cent. as against the value 10·68 per cent. required for pure indigotin. Calculating the nitrogen value found to indigotin, shows that the residues which, by direct weighing, indicated 70·34 and 69·34 per cent. of indigotin had in reality a mean value of only 63·69 per cent., so that, even after the prolonged process of extraction with acetic-sulphuric acid and methyl alcohol, a weighing of the final product on the assumption that it is pure indigotin involves an error of +6·15 per cent. of the true indigotin value as indicated by the estimation of the nitrogen by Kjeldahl's process.

The conclusion arrived at is, that although this method succeeds in the case of Rawson's standard, where the initial percentage of indigotin is over 90, yet in the case of ordinary cake indigo (containing 70 per cent. of indigotin and less) the prolonged series of extractions shown to be necessary is such as to render the process too tedious for the preparation of pure indigotin.

The Preparation of Pure Indigotin by Sublimation.

It has not been found possible to obtain pure indigotin by the sublimation of crude indigo in vessels open to the air. Various forms of apparatus were employed and the access of heat carefully regulated, but in all cases impure products were obtained, the sublimate con-

taining free carbon and products of destructive distillation. *Watts' Dictionary,* Vol. 3, p. 253, contains the following statement with regard to indigo: "In open vessels it volatilises at about 288° in dark purple red vapours." This is incorrect, for no purple vapours could be obtained on heating to the upper limit of the thermometers available (400°). Heating under diminished pressure, however, yielded a sublimate of pure indigotin in any desired quantity.

The crude indigo (dry and finely powdered) was placed in a long-necked Jena flask such as is used for digestion with acid in Kjeldahl's process, and this flask, which was imbedded in a protective metal vessel containing magnesia, was connected with a water-pump, a catch bottle being inserted between the flask and the pump. The pressure being reduced to about 100 mm., heat was applied, and at a red heat (600—800°) sublimation took place at less than an inch from the top of the crude indigo. The sublimate proved to be a beautifully crystalline powder, with a dark purple lustre, the powdered substance appearing almost black; no trace of impurity could be detected, a result which seemed to indicate that, before attaining the high temperature necessary for the sublimation of indigotin, the impurities originally present had, under the diminished pressure, passed off as gases, leaving the indigotin pure. The sublimed indigotin yielded the following results on analysis.

(1) *Estimation of Nitrogen by Kjeldahl's Method.*

Two nitrogen estimations gave N = 10·58 and 10·52 per cent. (mean value 10·55), as against 10·68 per cent. required by pure indigotin. On calculating the mean to indigotin a percentage value of 98·71 is deduced. These are the highest values for nitrogen obtained by the author from any specimen of indigotin, and, possibly with more attention to experimental details, the theoretical number might be obtained. This result affords also satisfactory evidence that Kjeldahl's method is applicable to the estimation of nitrogen in substances of the nature of indigotin.

(2) *Analysis by Extraction with Acetic-sulphuric Acid.*

		Grams.
Weight of dry indigotin taken	=	1·0547.
,, ,, ,, ,, recovered	=	1·0540.

This result indicates that of the indigotin originally taken 99·93 per cent. was recovered after solution in acetic-sulphuric acid (5 : 1), filtration, and subsequent hydrolysis of the indigotin monosulphate.

By this sublimation method, *pure indigotin* can therefore be prepared rapidly and in quantity from crude indigo. At present the yield from

this operation is not known, but it seems possible that it may be sufficiently high to justify the process being worked on a commercial scale. The object here, however, was to obtain pure indigotin to serve as a control for the many processes proposed for the analysis of indigo, over which any rigid check was hitherto impossible in the absence of pure indigotin to serve as standard. Owing, however, to the termination of the period of the author's engagement in India, attention could only be paid to one well-known method of analysis, namely, that based on the oxidation by potassium permanganate.

The Estimation of Indigotin by Potassium Permanganate.

This method has been employed in India almost exclusively, the rapidity of the process constituting its great attraction, but the most astonishingly widely divergent results have been obtained and published by investigators using it. The writer was, however, unable to obtain any concordant results when making analyses of ordinary cake indigo, or even when employing specimens of indigo of comparative purity, such as "B.A.S.F. Indigo pure" (91·88 per cent. indigotin) and "Indigotin by purchase" (90·85 per cent. indigotin). The difficulty was, in all cases, due to the impossibility of detecting the exact end-point.

Full directions for sulphonation and analysis are given by Knecht, Rawson, and Lowenthal (*loc. cit.*), the fundamental equation suggested by these authors being as follows:

$$5C_{16}H_8O_2N_2(HSO_3)_2 + 4KMnO_4 + 6H_2SO_4 = 5C_{16}H_8O_4N_2(HSO_3)_2 + 2K_2SO_4 + 4MnSO_4 + 6H_2O.$$

Consequently "316 parts of potassium permanganate are equivalent to 655 parts of indigotin," but it is stated that with a weaker solution of indigotin a smaller amount of permanganate is consumed than is indicated by the foregoing equation. In the directions * given by Rawson occurs the following statement: "each c.c. of $N/50$ permanganate [0·632 gram per litre] corresponds to 0·0015 of indigotin." As a comment on these directions, it may be observed, of Rawson's statement, that "in a strong solution of indigotin" the relation $\frac{\text{indigotin}}{\text{permanganate}} = \frac{655}{316} = \frac{2{\cdot}072}{1{\cdot}0}$ is found to hold good; whilst in the dilute solution, another relation, $\frac{\text{indigotin}}{\text{permanganate}} = \frac{1500}{632} = \frac{2{\cdot}373}{1{\cdot}0}$, is stated to exist. It seems, there-

* "0·5 gram of indigotin sulphonated by treatment with 20 c.c. concentrated sulphuric acid, dilute with water, make up to 500 c.c. and filter if necessary. Of this solution take 25 c.c. or 50 c.c. in a porcelain dish to which are added 250 c.c. of pure water."

fore, doubtful whether the oxidising power of permanganate should prove to be so much greater in a weaker solution. To test these statements, a solution of the sulphindigotic acid was made from the author's pure sublimed indigotin, and its analysis effected exactly according to Rawson's conditions. No impurities being present, the end reaction should be sharp and easily detected (as claimed by Rawson, *loc. cit.*), and 50 c.c. of the pure sulphindigotic acid (= 0·05 gram indigotin) should require 33·3 c.c. of *N*/50 solution of permanganate.

It was found, however, that no definite end reaction could be obtained relying on the eye alone, even when the titration limit had been exceeded by the addition of 50 c.c. of permanganate solution, and when the distinctly red liquid was left in the porcelain dish the colour due to permanganate soon disappeared, leaving a pure yellow solution. To obtain definite evidence of the continued reaction of the permanganate and sulphindigotic acid beyond the limits given by Rawson, the following experiment was carried out. A solution of potassium iodide was acidified with sulphuric acid of the strength used in Rawson's method of titration. This solution did not liberate iodine after standing in air, for it remained colourless even on the addition of starch solution. But this acidified solution of potassium iodide and starch was found to be sensitive to the addition of a few drops of a potassium permanganate solution, so dilute as to be almost colourless. With the aid of this iodide solution in detecting excess of permanganate, it was proved that although, to separate portions of the sulphindigotic acid, solution *N*/50 permanganate was added until the liquid was distinctly red, the amount being far in excess of Rawson's limit, yet the solutions, after a few minutes' standing, gave no indication of the presence of excess of permanganate, whilst their colour had reverted to pure yellow. Thus the failure to detect, by the eye, a definite termination of the reaction was explained. The futility of this process was revealed by another mode of experiment.

A solution of sulphindigotic acid was made from pure indigotin (obtained by sublimation, see p. 983), observing Rawson's conditions of concentration (see p. 984).

Three portions, of 50 c.c. each, of this solution (= 0·05 gram indigotin) were added to an excess of *N*/50 potassium permanganate solution, 150 c.c. being employed in each case, and to each was then added 250 c.c. of a 2 per cent. solution of pure sulphuric acid.

In each of these solutions, after 1, 15, and 30 minutes respectively, the excess of potassium permanganate was estimated by the liberation of iodine from potassium iodide and its titration by sodium thiosulphate with starch as indicator.

The results obtained were as follows :

(*a*) 50 c.c. soln. Sulphindigotic acid = 61·27 c.c. $N/50$ $KMnO_4$, after 1 minute.

(*b*) 50 c.c. soln. Sulphindigotic acid = 82·77 c.c. $N/50$ $KMnO_4$, after 15 minutes.

(*c*) 50 c.c. soln. Sulphindigotic acid = 98·42 c.c. $N/50$ $KMnO_4$, after 30 minutes.

Hence, although the indigotin value was the same in each experiment (50 c.c. = 0·05 gram indigotin), the amount of permanganate consumed increases with the duration of the experiment. Now if Rawson's value for the permanganate solution at the concentration prescribed by him be accepted as correct (1 c.c. $N/50$ $KMnO_4$ = 0·0015 gram indigotin), then the results above quoted will work out as follows:

(*a*) After 1 minute = 0·091 gram indigotin.
(*b*) ,, 15 minutes = 0·124 ,, ,,
(*c*) ,, 30 ,, = 0·148 ,, ,,

Whereas the quantity of indigotin involved was 0·05 gram in all three cases. Accordingly, the degrees of error involved will be

(*a*) = + 182 ; (*b*) = + 248 ; (*c*) = + 296 per cent.,

the amount of indigotin actually present (0·05 gram) being taken as 100·00 per cent.

The author maintains, therefore, that the method for analysis of indigo by sulphonation and titration with solution of potassium permanganate as at present conducted is altogether useless and misleading, even when pure indigotin is available and when the conditions of similar concentration can be observed. For, as has been shown, the oxidation is a progressive action, the end-point is at no time definite and sharp, and, by altering the conditions of experiment, errors varying from + 182 to + 296 per cent. can be obtained by it.

That a definite pronouncement is needed on the errors of the permanganate process for indigo analysis is shown by the publication of two papers at dates subsequent to the contribution of this paper to the Society (*Proc.*, 1904, **20**, 159). Bergtheil, on "The Fermentation of the Indigo-plant" (Trans., 1904, **85**, 870), employs the permanganate process on which to base all numerical data for enzyme action, and Grossmann, "An Improved Method of Indigo-testing" (*Journ. Soc. Chem. Ind.*, 1905, **24**, 308), recommends a slight modification of the permanganate process. It is the author's intention, with the aid of the pure indigotin now so readily obtained, to proceed with an examination into the accuracy of the other processes recommended for the analysis of indigo, for until an accurate analytical method (or methods) shall have been established, further progress in the many difficulties attend-

